

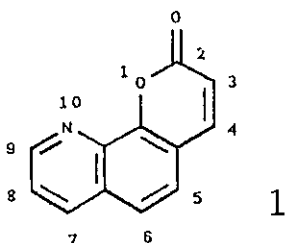
A SYNTHESIS OF 2-OXO-2H-PYRANO[2,3-*f*]QUINOLINE DERIVATIVES

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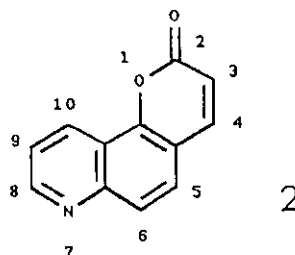
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Abstract - A synthesis of some derivatives of 2-oxo-2H-pyrano[2,3-*f*]quinoline from 5,8-quinolinequinone and dialkyl 2-aminofumarate is described.

2H-Pyrano[3,2-*h*]quinolin-2-ones (**1**) and 2H-pyrano[2,3-*f*]quinolin-2-ones (**2**) have been prepared from 8-hydroxy- and 5-hydroxyquinolines and their formyl derivatives according to the Knoevenagel's and Pechmann's methods with β -keto esters.¹⁻⁴ Similarly, 7,8,9,10-tetrahydropyrano[2,3-*f*]quinolin-2-ones have been prepared from the corresponding 5-hydroxy-1,2,3,4-tetrahydroquinoline.⁵



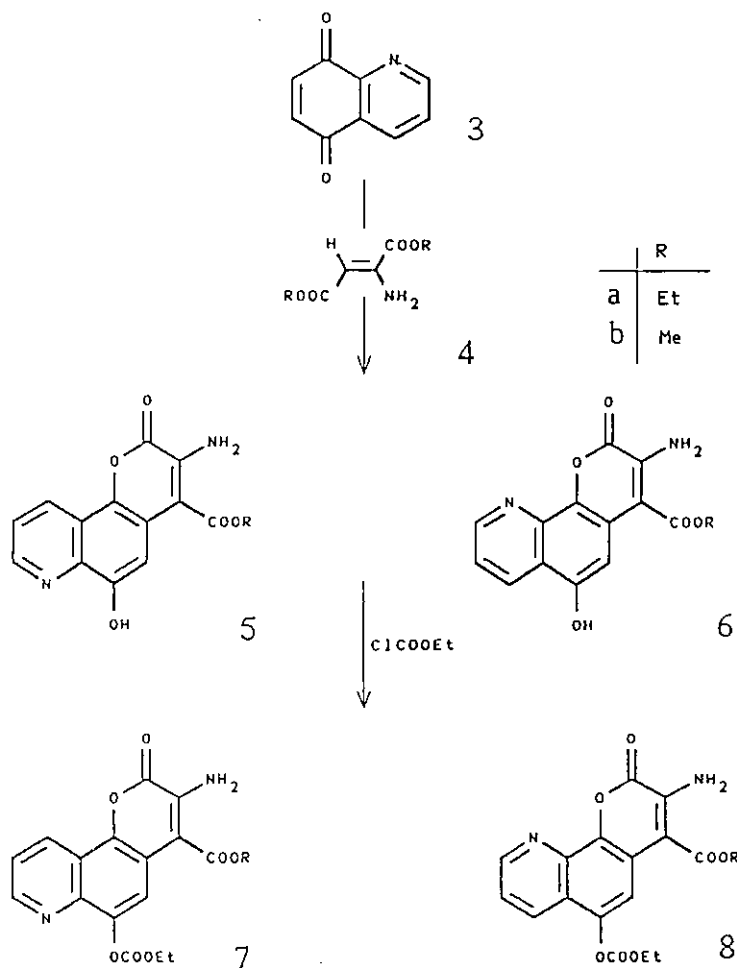
2H-Pyrano[3,2-*h*]quinolin-2-one



2H-Pyrano[2,3-*f*]quinolin-2-one

Dedicated to Professor Alan R. Katritzky, University of South Florida, USA, on the occasion of his 65th birthday.

Recently, pyranones and fused pyranones, such as benzopyranones, pyrano-benzopyranones, pyranoazoles, pyranoazines, isomeric naphthopyranones and naphthodipyrans, have been prepared from cyclic systems with an active methylene or potential methylene group as a part of the ring system and methyl 2-benzoylamino-3-dimethylaminopropenoate.⁶⁻⁸ On the other hand, 1,4-benzoquinone and 1,4-naphthoquinone react with diethyl and dimethyl 2-aminofumarates to give 4-alkoxycarbonyl-3-amino-6-hydroxy-2*H*-benzo[*b*]-pyran-2-one and the corresponding 2*H*-naphtho[1,2-*b*]pyran-2-one derivatives, respectively.⁹⁻¹²



Scheme 1

5,8-Quinolinequinone is nonsymmetrical. Therefore, the reaction with dialkyl 2-aminofumarates can proceed either at position 6 followed by cyclization in which the hydroxy group at position 5 is involved to give the tricyclic system (5) or at position 7 followed by cyclization in which the hydroxy group at position 8 is involved to give the isomeric system (6). The elemental analyses gave the molecular formula $C_{14}H_{10}N_2O_5$ for the methyl ester (5b) and $C_{15}H_{12}N_2O_5$ for the ethyl ester (5a). The molecular formula $C_{17}H_{14}N_2O_7$ for the compound 7b was confirmed also by high resolution mass spectrum.

The 1H nmr spectrum of the products show besides the ester alkyl groups a broad singlet at $\delta = 6.5-7.6$ ppm integrating for two protons, corresponding to amino group, a singlet at $\delta = 8.0$ ppm integrating for one proton corresponding to H_5 , three doublets of doublets at $\delta = 7.7-7.8$ ppm, $\delta = 8.7-8.8$ ppm and $\delta = 9.0-9.1$ ppm with coupling constants $J = 9.0$ Hz, $J = 4.5$ Hz and $J = 1.5$ Hz, corresponding to three protons at β -, γ - and α -position in the pyridine ring, respectively.

On the basis of these data it was not possible to differentiate between the isomeric structures 5 and 6. Therefore, the X-ray analysis of the compound obtained from 5,8-quinolinequinone and diethyl 2-aminofumarate was undertaken to show that the compound is the corresponding derivate of 2H-pyrano[2,3-f]quinolin-2-one (5a).

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EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. 1H nmr spectra were obtained on JEOL 90 Q FT and VARIAN E-360 instruments, and elemental

analyses for C, H, and N on a PERKIN-ELMER Analyzer 2400.

3-Amino-4-ethoxycarbonyl-6-hydroxy-2H-pyrano[2,3-f]quinolin-2-one (5a). -

A suspension of 3 (796 mg, 5. mmol) in acetic acid (2 ml) was added slowly during stirring to diethyl 2-aminofumarate (4a) (990 mg, 5.3 mmol) at 0°C. The mixture was left for 24 h at room temperature and the precipitate was collected by filtration to give crude product (375 mg, 25 %), which was purified by sublimation at 200°C, mp 241-243°C, ¹H nmr (90 MHz, DMSO-d₆) δ: 1.4 (3H, t, J_{CH-CH} = 7.0 Hz, MeCH₂OCO), 4.6 (2H, q, J_{CH-CH} = 7.0 Hz, MeCH₂OCO), 7.5 (2H, br s, NH₂), 7.8 (1H, dd, J_{H9-H10} = 9.0 Hz, J_{H8-H9} = 4.5 Hz, H₉), 8.0 (1H, s, H₅), 8.8 (1H, dd, J_{H9-H10} = 9.0 Hz, J_{H8-H10} = 1.5 Hz, H₁₀), 9.1 (1H, dd, J_{H8-H9} = 4.5 Hz, J_{H8-H10} = 1.5 Hz, H₈), 10.0 (1H, br s, OH). Anal. Calcd for C₁₅H₁₂N₂O₅: C, 60.00; H, 4.03; N, 9.33. Found: C, 59.85; H, 4.19; N, 9.62.

3-Amino-6-hydroxy-4-methoxycarbonyl-2H-pyrano[2,3-f]quinolin-2-one (5b).

- This compound was prepared in the same manner as 5a from 3 and dimethyl 2-aminofumarate (4b) in 31 % yield, mp > 260°C (from a mixture of DMSO and ethanol), ¹H nmr (90 MHz, DMSO-d₆) δ: 4.1 (3H, s, COOMe), 6.6 - 7.6 (2H, br s, NH₂), 7.7 (1H, dd, J_{H9-H10} = 9.0 Hz, J_{H8-H9} = 4.5 Hz, H₉), 8.0 (1H, s, H₅), 8.7 (1H, dd, J_{H9-H10} = 9.0 Hz, J_{H8-H10} = 3.0 Hz, H₁₀), 9.0 (1H, dd, J_{H8-H9} = 4.5 Hz, J_{H8-H10} = 3.0 Hz, H₈). Anal. Calcd for C₁₄H₁₀N₂O₅: C, 58.75; H, 3.52; N, 9.79. Found: C, 58.87; H, 3.42; N, 9.67.

3-Amino-4-ethoxycarbonyl-6-ethoxycarbonyloxy-2H-pyrano[2,3-f]quinolin-2-one (7a). -

Ethyl chloroformate (0.1 ml, 1 mmol) was added slowly during stirring to a solution of 5a (300 mg, 1 mmol) in pyridine (3 ml, 37 mmol). The mixture was left at room temperature for 3 days. The solution was then poured into water (2 ml) and methanol was added dropwise until yellow crystals were formed. The precipitate was collected by filtration to give 7a (290 mg, 78 %), mp 191-198°C (from benzene), ¹H nmr (90 MHz,

CDCl₃) δ : 1.5 (3H, t, $J_{\text{CH-CH}} = 7.0$ Hz, MeCH_2OCO), 1.6 (3H, t, $J_{\text{CH-CH}} = 7.0$ Hz, MeCH_2OCOO), 4.5 (2H, q, $J_{\text{CH-CH}} = 7.0$ Hz, MeCH_2OCO), 4.6 (2H, q, $J_{\text{CH-CH}} = 7.0$ Hz, MeCH_2OCOO), 7.2 (2H, br s, NH_2), 7.7 (1H, dd, $J_{\text{H}_9\text{-H}_{10}} = 8.0$ Hz, $J_{\text{H}_8\text{-H}_9} = 4.0$ Hz, H_9), 8.8 (1H, s, H_5), 8.9 (1H, dd, $J_{\text{H}_9\text{-H}_{10}} = 8.0$ Hz, $J_{\text{H}_8\text{-H}_{10}} = 2.0$ Hz, H_{10}), 9.1 (1H, dd, $J_{\text{H}_8\text{-H}_9} = 4.0$ Hz, $J_{\text{H}_8\text{-H}_{10}} = 2.0$ Hz, H_8). Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_7$: C, 58.07; H, 4.33; N, 7.52. Found: C, 58.43; H, 4.39; N, 7.39.

3-Amino-6-ethoxycarbonyloxy-4-methoxycarbonyl-2H-pyrano[2,3-f]quinolin-2-one (7b). - This compound was prepared in the same manner from ethyl

chloroformate and **5b** in 52 % yield, mp 219-220°C (from a mixture of chloroform and ethanol), ms 358.081, 358 (M^+ , 43%), base peak (100). ^1H nmr (90 MHz, DMSO- d_6) δ : 1.4 (3H, t, $J_{\text{CH-CH}} = 8.5$ Hz, MeCH_2OCOO), 4.0 (3H, s, COOMe), 4.4 (2H, q, $J_{\text{CH-CH}} = 8.5$ Hz, MeCH_2OCOO), 7.6-8.0 (3H, dd and br s overlapped, $J_{\text{H}_9\text{-H}_{10}} = 10.0$ Hz, $J_{\text{H}_8\text{-H}_9} = 4.5$ Hz, H_9 and NH_2), 8.6 (1H, s, H_5), 8.9 (1H, dd, $J_{\text{H}_9\text{-H}_{10}} = 10.0$ Hz, $J_{\text{H}_8\text{-H}_{10}} = 2.0$ Hz, H_{10}), 9.1 (1H, dd, $J_{\text{H}_8\text{-H}_9} = 4.5$ Hz, $J_{\text{H}_8\text{-H}_{10}} = 2.0$ Hz, H_8). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_7$: C, 56.98; H, 3.94; N, 7.82. Found: C, 56.98; H, 3.92; N, 7.65.

X-ray structure determination. - Crystal data: $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5$, $M = 300.27$, triclinic, $P1$, $a = 10.591(1)$, $b = 12.040(1)$, $c = 12.078(1)$ Å, $\alpha = 68.85(1)$, $\beta = 85.12(1)$, $\gamma = 65.68(1)^\circ$, $V = 1305.3(6)$ Å³, $Z = 4$, $D_x = 1.528$ Mg m⁻³, MoK α radiation $\lambda = 0.71069$ Å, $\mu = 0.109$ mm⁻¹, $F(000) = 624$, $T = 293(2)$ K.

An approximate prismatic crystal with the dimensions $0.15 \times 0.29 \times 0.53$ mm was used for data collection on an ENRAF-NONIUS CAD-4 diffractometer with graphite monochromatized MoK α radiation. Lattice parameters were determined by a least-squares treatment of 100 centred θ values in the range $10 < \theta < 15^\circ$. Entire sphere to $\theta_{\text{max}} 28^\circ$ of data was measured with an index range $-13 \leq h \leq 13$, $-15 \leq k \leq 15$ and $-15 \leq l \leq 15$ at room

temperature (293(2) K) by the $\omega - 2\theta$ scan technique with a minimum and maximum scan rate of 1.04 and 5.55 °/min and a scan width $(0.8 + 0.3 \times \tan \theta)^\circ$ with aperture $(2.4 + 0.9 \times \tan \theta)$ mm, maximum scan time 60 s. Background intensities were measured at 1/4 of the scan at each limit. Crystal stability was monitored by measuring of three standard reflections (2,-4,-3; -4,-3,-6; 5,3,-2) every 20000 s of scanning time. A change of +3.34% intensities of standard reflections was observed and a correction applied. No absorption correction was done. 12806 reflections were collected, averaging gave 6263 unique reflections with R_{int} 0.016, 3349 of them were observed ($I > 2.5\sigma(I)$).

The structure was solved by direct methods using MULTAN80¹³ system of computer programs. All hydrogen atoms were located on an intermediate difference map and were refined with isotropic thermal factors. Their positions do not differ significantly from idealised positions. Five blocks matrix least-squares refinement on F magnitudes with anisotropic temperature factors for all nonhydrogen atoms, using the empirical weighting function $w = 6.0 \times W_f \times W_g$ where $W_f(|F_o| < 4.0) = (|F_o|/4.0)^2$, $W_f(|F_o| > 7.0) = (7.0/|F_o|)^{1.5}$, $W_f(4.0 < |F_o| < 7.0) = 1.0$ and $W_g(\sin \theta < 0.35) = \sin \theta / 0.35$, $W_g(\sin \theta > 0.45) = (0.45 / \sin \theta)^2$, $W_g(0.35 < \sin \theta < 0.45) = 1.0$ to keep $\sum w(\Delta F)^2$ uniform over the ranges of $\langle \sin \theta / \lambda \rangle$ and $\langle F_o \rangle$. In the final least-squares cycle were 4365 (m) contributing reflections (included were those unobserved reflections for which F_c was greater than F_o) and 493 (n) refined parameters, data-to-variable ratio (m/n) 8.8, scale factor 0.983, $S = (\sum w(\Delta F)^2 / (m-n))^{1/2}$ 0.97, average and maximum shift/error 0.074 and 1.7 at scale factor, residual density in final difference map was max. 0.36 and min. -0.27 e/Å³. The final R and R_w are 0.039 and 0.053, respectively. Atomic scattering factors for neutral atoms^{14,15} and dispersion corrections¹⁶ were used. All calculations were performed on the DEC-10 computer at University Computer Center Ljubljana using

XRAY76¹⁷ system of crystallographic programs.

The compound has in asymmetric unit two formula units with small differences in interatomic distances and angles. The most significant difference is in torsion angles C(11)-O(5)-C(12)-C(13) and C(11')-O(5')-C(12')-C(13') with values $-167.7(2)$ and $-98.9(2)^\circ$. Minimum-overlap view of the asymmetric unit with atom-numbering scheme is shown in Fig. 1. Final atomic coordinates and equivalent isotropic thermal parameters along with their e.s.d.'s are listed in Table 1. Interatomic distances and angles are presented in Table 2. List of structure factors, anisotropic thermal parameters and hydrogen atoms parameters are available from the author L.G. Molecules are connected to a chain by weak hydrogen bonds O(2)...H-N(3'), N(3)-H...O(2') and N(7)...H-O(6'), O(6)-H...N(7').

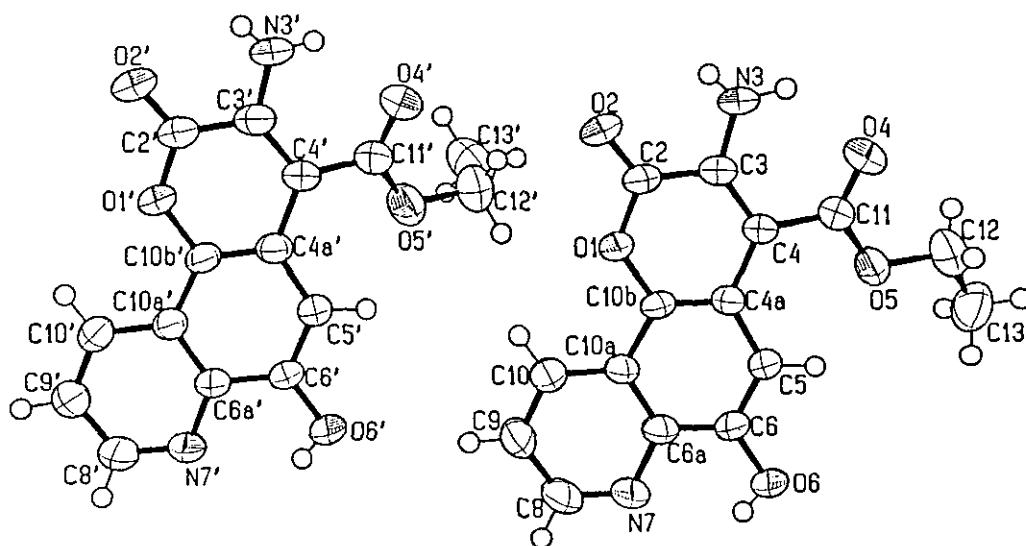


Figure 1. Minimum-overlap view of the asymmetric unit

Table 1. Fractional Coordinates ($\times 10^4$) and Equivalent Temperature Factors, U_{eq} ($\text{\AA}^2 \times 10^3$) of 5a

	x	y	z	U_{eq}
O(1)	1392(1)	4071(1)	2355(1)	59(1)
C(2)	703(2)	4940(2)	2881(2)	56(1)
O(2)	1373(1)	5185(1)	3445(1)	85(1)
C(3)	-832(2)	5532(2)	2743(1)	52(1)
N(3)	-1393(2)	6390(2)	3291(2)	85(1)
C(4)	-1532(2)	5162(2)	2124(1)	44(1)
C(11)	-3068(2)	5755(2)	2092(2)	51(1)
O(4)	-3730(1)	6692(1)	2382(1)	84(1)
O(5)	-3697(1)	5166(1)	1746(1)	68(1)
C(12)	-5212(2)	5721(2)	1714(2)	73(1)
C(13)	-5693(2)	4779(2)	1573(2)	80(1)
C(4a)	-721(1)	4236(1)	1544(1)	39(1)
C(5)	-1282(2)	3818(2)	816(1)	46(1)
C(6)	-449(2)	2986(2)	268(1)	47(1)
O(6)	-1055(1)	2640(1)	-422(1)	77(1)
C(6a)	1022(2)	2499(1)	403(1)	43(1)
N(7)	1799(1)	1687(1)	-180(1)	57(1)
C(8)	3158(2)	1276(2)	-53(2)	77(1)
C(9)	3844(2)	1601(2)	646(2)	83(1)
C(10)	3071(2)	2403(2)	1244(2)	67(1)
C(10a)	1613(2)	2886(1)	1126(1)	45(1)
C(10b)	709(1)	3747(1)	1675(1)	45(1)
O(1')	10274(1)	1525(1)	4147(1)	52(1)
C(2')	9617(2)	2428(2)	4647(1)	52(1)
O(2')	10312(1)	2768(1)	5087(1)	80(1)
C(3')	8084(2)	2932(2)	4647(1)	51(1)
N(3')	7544(2)	3823(2)	5167(2)	79(1)
C(4')	7376(2)	2426(2)	4193(1)	46(1)
C(11')	5906(2)	2765(2)	4442(1)	54(1)
C(12')	4036(2)	2071(2)	4748(2)	78(1)
O(4')	5184(1)	3705(2)	4706(1)	85(1)
O(5')	5440(1)	1895(1)	4412(1)	71(1)
C(13')	4086(3)	1212(2)	5996(2)	91(1)
C(4a')	8135(2)	1561(1)	3548(1)	44(1)
C(5')	7499(2)	1169(2)	2847(1)	53(1)
C(6')	8265(2)	386(2)	2234(1)	52(1)
O(6')	7608(1)	60(1)	1564(1)	82(1)
C(6a')	9744(2)	-89(1)	2298(1)	45(1)
N(7')	10461(1)	-897(1)	1693(1)	59(1)
C(8')	11825(2)	-1316(2)	1759(2)	70(1)
C(9')	12573(2)	-1003(2)	2413(2)	63(1)
C(10')	11871(2)	-192(2)	3018(2)	50(1)
C(10a')	10398(2)	299(1)	2969(1)	40(1)
C(10b')	9553(2)	1142(1)	3555(1)	43(1)

Table 2a. Bond distances (Å) with e.s.d.'s in parentheses

O(1) - C(2)	1.343(2)	O(1') - C(2')	1.345(2)
C(2) - C(3)	1.479(2)	C(2') - C(3')	1.481(2)
C(2) - O(2)	1.206(3)	C(2') - O(2')	1.209(3)
C(3) - C(4)	1.383(3)	C(3') - C(4')	1.387(3)
C(3) - N(3)	1.334(3)	C(3') - N(3')	1.339(3)
C(4) - C(11)	1.481(2)	C(4') - C(11')	1.472(2)
C(4) - C(4a)	1.463(2)	C(4') - C(4a')	1.458(2)
C(4a) - C(5)	1.426(3)	C(4a') - C(5')	1.428(3)
C(4a) - C(10b)	1.381(2)	C(4a') - C(10b')	1.374(2)
C(5) - C(6)	1.368(2)	C(5') - C(6')	1.367(3)
C(6) - C(6a)	1.422(2)	C(6') - C(6a')	1.428(2)
C(6) - O(6)	1.357(3)	C(6') - O(6')	1.358(3)
C(6a) - N(7)	1.365(2)	C(6a') - N(7')	1.367(2)
C(6a) - C(10a)	1.413(3)	C(6a') - C(10a')	1.410(3)
N(7) - C(8')	1.318(2)	N(7') - C(8')	1.318(2)
C(8) - C(9)	1.404(4)	C(8') - C(9')	1.400(4)
C(9) - C(10)	1.370(3)	C(9') - C(10')	1.366(3)
C(10) - C(10a)	1.408(2)	C(10') - C(10a')	1.420(2)
C(10a) - C(10b)	1.415(2)	C(10a') - C(10b')	1.413(2)
O(1) - C(10b)	1.383(3)	O(1') - C(10b')	1.388(3)
C(11) - O(4)	1.216(3)	C(11') - O(4')	1.214(3)
C(11) - O(5)	1.332(3)	C(11') - O(5')	1.341(3)
O(5) - C(12)	1.460(2)	C(12') - O(5')	1.457(3)
C(12) - C(13)	1.484(4)	C(12') - C(13')	1.479(3)

Table 2b. Bond angles (°) with e.s.d.'s in parentheses

C(10b) - O(1) - C(2)	122.0(1)	C(10b') - O(1') - C(2')	121.9(1)
O(2) - C(2) - O(1)	118.1(2)	O(2') - C(2') - O(1')	118.2(2)
C(3) - C(2) - O(1)	118.0(2)	C(3') - C(2') - O(1')	118.1(2)
C(4a) - C(10b) - O(1)	122.5(1)	C(4a') - C(10b') - O(1')	122.0(1)
C(10a) - C(10b) - O(1)	113.7(1)	C(10a') - C(10b') - O(1')	114.4(2)
C(3) - C(2) - O(2)	123.9(2)	C(3') - C(2') - O(2')	123.6(2)
N(3) - C(3) - C(2)	112.3(2)	N(3') - C(3') - C(2')	112.9(2)
C(4) - C(3) - C(2)	120.6(2)	C(4') - C(3') - C(2')	119.9(2)
C(4) - C(3) - N(3)	127.0(2)	C(4') - C(3') - N(3')	127.1(2)
C(11) - C(4) - C(3)	116.6(2)	C(11') - C(4') - C(3')	116.9(2)
C(4a) - C(4) - C(3)	118.6(2)	C(4a') - C(4') - C(3')	118.6(2)
C(4a) - C(4) - C(11)	124.8(2)	C(4a') - C(4') - C(11')	124.4(2)
O(4) - C(11) - C(4)	123.7(2)	O(4') - C(11') - C(4')	124.1(2)
O(5) - C(11) - C(4)	115.1(2)	O(5') - C(11') - C(4')	113.6(2)
C(5) - C(4a) - C(4)	125.6(2)	C(5') - C(4a') - C(4')	124.5(2)
C(10b) - C(4a) - C(4)	118.0(1)	C(10b') - C(4a') - C(4')	118.5(2)
O(5) - C(11) - O(4)	121.2(2)	O(5') - C(11') - O(4')	122.2(2)
C(12) - O(5) - C(11)	116.4(2)	C(12') - O(5') - C(11')	118.3(2)
C(13) - C(12) - O(5)	108.2(2)	C(13') - C(12') - O(5')	109.7(2)
C(10b) - C(4a) - C(5)	116.4(1)	C(10b') - C(4a') - C(5')	117.0(2)
C(6) - C(5) - C(4a)	121.9(2)	C(6') - C(5') - C(4a')	121.7(2)
C(10a) - C(10b) - C(4a)	123.7(2)	C(10a') - C(10b') - C(4a')	123.6(2)
O(6) - C(6) - C(5)	118.7(2)	O(6') - C(6') - C(5')	119.4(2)
C(6a) - C(6) - C(5)	121.1(2)	C(6a') - C(6') - C(5')	120.4(2)

C(6a) - C(6) - O(6)	120.2(2)	C(6a') - C(6') - O(6')	120.2(2)
N(7) - C(6a) - C(6)	118.4(2)	N(7') - C(6a') - C(6')	117.9(2)
C(10a) - C(6a) - C(6)	118.5(2)	C(10a') - C(6a') - C(6')	119.0(2)
C(10a) - C(6a) - N(7)	123.0(2)	C(10a') - C(6a') - N(7')	123.0(2)
C(8) - N(7) - C(6a)	116.7(2)	C(8') - N(7') - C(6a')	116.9(2)
C(10) - C(10a) - C(6a)	117.9(2)	C(10') - C(10a') - C(6a')	117.8(2)
C(10b) - C(10a) - C(6a)	118.4(2)	C(10b') - C(10a') - C(6a')	118.2(2)
C(9) - C(8) - N(7)	124.6(2)	C(9') - C(8') - N(7')	124.5(2)
C(10) - C(9) - C(8)	119.0(2)	C(10') - C(9') - C(8')	119.3(2)
C(10a) - C(10) - C(9)	118.8(2)	C(10a') - C(10') - C(9')	118.5(2)
C(10b) - C(10a) - C(10)	123.7(2)	C(10b') - C(10a') - C(10')	124.1(2)

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