4-HYDROXY-2-QUINOLONES. 43.* THERMOLYSIS OF ETHYL ESTERS OF 1-R-2-OXO-4-HYDROXY-QUINOLINE-3-CARBOXYLIC ACIDS

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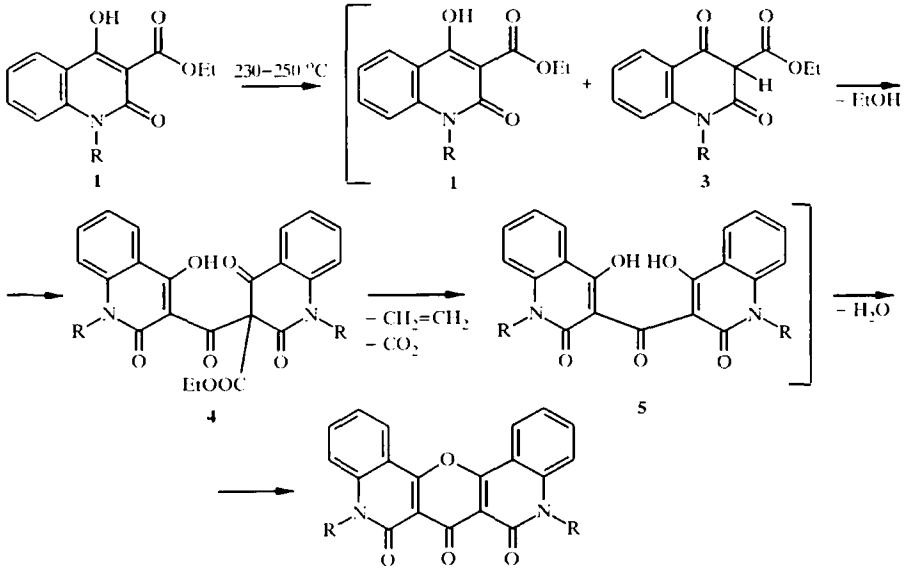
Ethyl esters of 1-R-2-oxo-4-hydroxyquinoline-3-carboxylic acids under thermolysis conditions are converted to 5,9-di-R-6,7,8-trioxodiquinolino[3,4-b;3',4'-e]-4H-pyrans. One of the synthesized compounds was studied by X-ray diffraction.

Keywords: 3-carbethoxy-4-hydroxy-2-quinolone, quinolinopyran, thermolysis, X-ray diffraction analysis.

We earlier noted the possibility of carrying out a Claisen condensation [2] and its intramolecular version, the Dieckmann reaction [3] under thermolysis conditions without using basic catalysts. Another interesting example of thermally activated ester condensation is thermolysis of ethyl esters of 1-R-2-oxo-4-hydroxyquinoline-3-carboxylic acids **1**.



2 a R = H, b R = Me, c R = Et

* For Communication 42, see [1].

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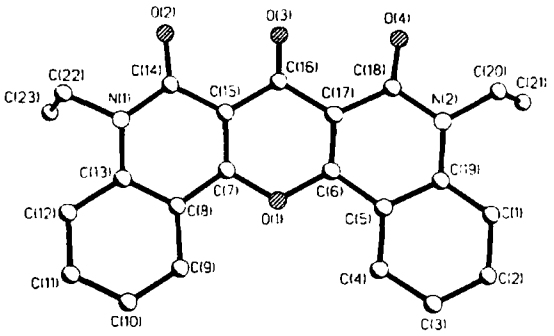

Fig. 1. Structure of compound **2c**.

As we found, when they are heated up to 230-250°C, novel products can be obtained in high yields whose formation, according to mass spectrometry, involves at least two molecules of the starting ester; and judging from the ^{1}H NMR spectra, these compounds have a symmetric structure. X-ray diffraction on the N-ethyl derivative confirmed these data and furthermore allowed us to establish that the compounds under study are 5,9-di-R-6,7,8-trioxodiquinolino[3,4-*b*;3',4'-*e*]-4H-pyrans **2**. Formation of such condensed systems obviously can be explained by the ability of 4-hydroxy-2-quinolones to exist in different tautomeric forms at elevated temperatures [4]. A significant contribution to the resonance hybrid from one of these (the 2,4-dioxo form **3**) is responsible for the possibility of intermolecular acylation, leading to carbonyldiquinoline **4**, after which the usual pyrolytic decomposition of the second ethoxycarbonyl group (probably as ethylene and CO_2 [5]) and subsequent irreversible closure of the pyran ring follow.

X-ray diffraction (Tables 1-3) established that in independent parts of the unit cell of the crystal of compound **2c**, there are two molecules (A and B) which differ in the structure of the pyran and pyridone moieties. The pyridone rings of molecule B are flat, while in molecule A they are found in a sofa conformation (the deviations of the $C_{(14)}$ and $C_{(18)}$ atoms from the mean-square planes of the rest of the atoms of the ring are 0.06 Å and -0.07 Å respectively). The pyran rings of both molecules are found in the boat conformation, but with different degrees of puckering. The deviations of the $C_{(16)}$ and $O_{(1)}$ atoms from the mean-square planes of the rest of the atoms of the ring are -0.09 Å (A), -0.17 Å (B) and -0.05 Å (A), -0.08 Å (B) respectively. The $O_{(2)}$, $O_{(4)}$, and $O_{(3)}$ atoms deviate in opposite directions relative to the mean plane of both molecules.

The ethyl groups are rotated relative to the $C_{(19)}$–$N_{(2)}$ and $C_{(13)}$–$N_{(1)}$ bonds (torsional angles $C_{(19)}$–$N_{(2)}$–$C_{(20)}$–$C_{(21)}$ 82.3(3)° (A), 90.2(2)° (B), $C_{(13)}$–$N_{(1)}$–$C_{(22)}$–$C_{(23)}$ -75.1(2)° (A), -80.8(3)° (B)).

Repulsion between alkyl substituents on the $N_{(1)}$, $N_{(2)}$ and $O_{(2)}$, $O_{(4)}$ atoms (shortened intramolecular contacts $H_{(22a)}$...$O_{(2)}$ 2.26 Å (A), 2.01 Å (B), $H_{(20b)}$...$O_{(4)}$ 2.30 Å (A), 2.31 Å (B), sum of the van der Waals radii 2.45 Å [6]) leads to lengthening of the bonds $N_{(1)}$–$C_{(13)}$ 1.390(2) Å (A), 1.389(3) Å (B), $N_{(2)}$–$C_{(19)}$ 1.393(3) Å (A), 1.388(3) Å (B) compared with the mean value 1.371 Å [7] and $N_{(1)}$–$C_{(14)}$ 1.398(3) Å (A), 1.397(3) Å (B), $N_{(2)}$–$C_{(18)}$ 1.397(3) Å (A), 1.400(3) Å (B) (mean value 1.355 Å). Similar effects have been observed in other N-alkyl derivatives of 2-quinoline [8].

EXPERIMENTAL

The ^{1}H NMR spectra of the synthesized compounds were recorded on a Bruker WP-100 SY in DMSO-d_6, internal standard TMS. The mass spectra were recorded on a Finnigan MAT Incos 50 quadrupole spectrometer in full scanning mode in the range 33-700 *m/z*, ionization by electron impact at 70 eV, direct injection, heating rate ~5°C/sec. The ethyl esters of 1-R-2-oxo-4-hydroxyquinoline-3-carboxylic acids **1a-c** were obtained by the procedure in [9].

TABLE 1. Coordinates of Non-hydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$\times 10^3$) in the Pyran **2c** Structure

Atom	x	y	z	U_{eq}
$N_{(1)}$	8413(2)	11673(2)	4479(1)	40(1)
$N_{(2)}$	11260(2)	7774(2)	2006(1)	44(1)
$O_{(1)}$	8781(1)	8406(1)	3530(1)	42(1)
$O_{(2)}$	9897(2)	12589(2)	3760(2)	63(1)
$O_{(3)}$	10688(2)	11017(2)	2444(2)	80(1)
$O_{(4)}$	11784(2)	9542(2)	1682(2)	64(1)
$C_{(1)}$	10622(2)	5788(2)	2239(2)	49(1)
$C_{(2)}$	9871(2)	4927(2)	2582(2)	55(1)
$C_{(3)}$	8988(2)	5109(2)	3031(2)	56(1)
$C_{(4)}$	8872(2)	6177(2)	3155(2)	49(1)
$C_{(5)}$	9635(2)	7080(2)	2824(2)	39(1)
$C_{(6)}$	9594(2)	8247(2)	2985(2)	36(1)
$C_{(7)}$	8721(2)	9525(2)	3832(2)	37(1)
$C_{(8)}$	7901(2)	9599(2)	4465(2)	37(1)
$C_{(9)}$	7237(2)	8619(2)	4776(2)	43(1)
$C_{(10)}$	6444(2)	8730(2)	5367(2)	48(1)
$C_{(11)}$	6290(2)	9817(2)	5670(2)	49(1)
$C_{(12)}$	6928(2)	10797(2)	5391(2)	45(1)
$C_{(13)}$	7749(2)	10705(2)	4779(2)	38(1)
$C_{(14)}$	9284(2)	11658(2)	3919(2)	42(1)
$C_{(15)}$	9396(2)	10473(2)	3542(2)	39(1)
$C_{(16)}$	10184(2)	10283(2)	2839(2)	45(1)
$C_{(17)}$	10290(2)	9106(2)	2636(2)	39(1)
$C_{(18)}$	11155(2)	8853(2)	2067(2)	44(1)
$C_{(19)}$	10512(2)	6880(2)	2342(2)	40(1)
$C_{(20)}$	12258(2)	7630(2)	1597(2)	57(1)
$C_{(21)}$	11833(3)	6687(3)	414(2)	82(1)
$C_{(22)}$	8181(2)	12781(2)	4738(2)	50(1)
$C_{(23)}$	6999(2)	12431(3)	3985(2)	63(1)
$N_{(1')}$	6395(2)	5358(2)	6986(1)	44(1)
$N_{(2')}$	3210(2)	951(2)	9313(1)	43(1)
$O_{(1')}$	3850(1)	3983(1)	8525(1)	42(1)
$O_{(2')}$	6714(2)	3629(2)	6586(2)	64(1)
$O_{(3')}$	5187(1)	1647(2)	7024(1)	51(1)
$O_{(4')}$	4583(2)	568(2)	8490(2)	69(1)
$C_{(1')}$	1748(2)	1369(2)	10225(2)	51(1)
$C_{(2')}$	1196(2)	2105(2)	10553(2)	58(1)
$C_{(3')}$	1439(2)	3151(2)	10314(2)	55(1)
$C_{(4')}$	2261(2)	3457(2)	9739(2)	46(1)
$C_{(5')}$	2843(2)	2715(2)	9384(2)	37(1)
$C_{(6')}$	3668(2)	2953(2)	8747(2)	36(1)
$C_{(7')}$	4690(2)	4371(2)	7986(2)	37(1)
$C_{(8')}$	4901(2)	5548(2)	7930(2)	39(1)
$C_{(9')}$	4283(2)	6225(2)	8368(2)	46(1)
$C_{(10')}$	4534(2)	7357(2)	8299(2)	55(1)
$C_{(11')}$	5426(2)	7845(2)	7813(2)	55(1)
$C_{(12')}$	6049(2)	7211(2)	7391(2)	50(1)
$C_{(13')}$	5793(2)	6037(2)	7426(2)	42(1)
$C_{(14')}$	6160(2)	4179(2)	6998(2)	43(1)
$C_{(15')}$	5247(2)	3679(2)	7540(2)	38(1)
$C_{(16')}$	4926(2)	2436(2)	7587(2)	38(1)
$C_{(17')}$	4205(2)	2218(2)	8359(2)	38(1)
$C_{(18')}$	4034(2)	1187(2)	8697(2)	45(1)
$C_{(19')}$	2600(2)	1656(2)	9636(2)	40(1)
$C_{(20')}$	3003(2)	-123(2)	9603(2)	52(1)
$C_{(21')}$	1978(3)	-1370(2)	8736(2)	73(1)
$C_{(22')}$	7341(2)	5872(3)	6469(2)	60(1)
$C_{(23')}$	6795(3)	5597(3)	5305(2)	72(1)

TABLE 2. Bond Lengths (l) in the Pyran **2c** Structure

Bond	l, Å	Bond	l, Å
$N_{(1)}$–$C_{(13)}$	1.390(2)	$N_{(1)}$–$C_{(14)}$	1.398(3)
$N_{(1')}$–$C_{(22')}$	1.475(3)	$N_{(2)}$–$C_{(19)}$	1.393(3)
$N_{(2')}$–$C_{(18')}$	1.397(3)	$N_{(2')}$–$C_{(20')}$	1.474(3)
$O_{(1)}$–$C_{(16)}$	1.360(2)	$O_{(1')}$–$C_{(17')}$	1.363(2)
$O_{(2)}$–$C_{(14)}$	1.220(2)	$O_{(3)}$–$C_{(16)}$	1.217(2)
$O_{(4)}$–$C_{(18)}$	1.220(2)	$C_{(1)}$–$C_{(2)}$	1.374(3)
$C_{(1)}$–$C_{(19)}$	1.401(3)	$C_{(2)}$–$C_{(3)}$	1.381(3)
$C_{(3)}$–$C_{(4)}$	1.369(3)	$C_{(4)}$–$C_{(5)}$	1.402(3)
$C_{(5)}$–$C_{(19)}$	1.403(3)	$C_{(5)}$–$C_{(6)}$	1.434(3)
$C_{(6)}$–$C_{(17)}$	1.353(3)	$C_{(7)}$–$C_{(15)}$	1.367(3)
$C_{(7)}$–$C_{(8)}$	1.420(3)	$C_{(8)}$–$C_{(13)}$	1.410(3)
$C_{(8)}$–$C_{(9)}$	1.411(3)	$C_{(9)}$–$C_{(10)}$	1.363(3)
$C_{(10)}$–$C_{(11)}$	1.388(3)	$C_{(11)}$–$C_{(12)}$	1.374(3)
$C_{(12)}$–$C_{(13)}$	1.406(3)	$C_{(14)}$–$C_{(15)}$	1.473(3)
$C_{(15)}$–$C_{(16)}$	1.477(3)	$C_{(16)}$–$C_{(17)}$	1.477(3)
$C_{(17)}$–$C_{(18)}$	1.472(3)	$C_{(20)}$–$C_{(21)}$	1.504(4)
$C_{(22')}$–$C_{(23')}$	1.512(3)	$N_{(1')}$–$C_{(13')}$	1.389(3)
$N_{(1')}$–$C_{(14')}$	1.397(3)	$N_{(1')}$–$C_{(22')}$	1.478(3)
$N_{(2')}$–$C_{(19')}$	1.388(3)	$N_{(2')}$–$C_{(18')}$	1.400(3)
$N_{(2')}$–$C_{(20')}$	1.473(3)	$O_{(1')}$–$C_{(17')}$	1.369(2)
$O_{(1')}$–$C_{(16')}$	1.370(2)	$O_{(2')}$–$C_{(14')}$	1.219(3)
$O_{(3')}$–$C_{(16')}$	1.213(2)	$O_{(4')}$–$C_{(18')}$	1.222(3)
$C_{(1')}$–$C_{(2')}$	1.359(3)	$C_{(1')}$–$C_{(19')}$	1.407(3)
$C_{(2')}$–$C_{(3')}$	1.389(3)	$C_{(3')}$–$C_{(4')}$	1.369(3)
$C_{(4')}$–$C_{(5')}$	1.401(3)	$C_{(5')}$–$C_{(19')}$	1.415(3)
$C_{(5')}$–$C_{(6')}$	1.423(3)	$C_{(6')}$–$C_{(17')}$	1.356(3)
$C_{(7')}$–$C_{(15')}$	1.357(3)	$C_{(7')}$–$C_{(8')}$	1.428(3)
$C_{(8')}$–$C_{(9')}$	1.404(3)	$C_{(8')}$–$C_{(13')}$	1.412(3)
$C_{(9')}$–$C_{(10')}$	1.369(3)	$C_{(10')}$–$C_{(11')}$	1.393(3)
$C_{(11')}$–$C_{(12')}$	1.367(3)	$C_{(12')}$–$C_{(13')}$	1.400(3)
$C_{(14')}$–$C_{(15')}$	1.470(3)	$C_{(15')}$–$C_{(16')}$	1.477(3)
$C_{(16')}$–$C_{(17')}$	1.480(3)	$C_{(17')}$–$C_{(18')}$	1.470(3)
$C_{(20')}$–$C_{(21')}$	1.501(3)	$C_{(22')}$–$C_{(23')}$	1.518(4)

6,7,8-Trioxodiquinolino[3,4-*b*; 3',4'-*e*]-4H-pyran (2a). Ethyl ester of 1H-2-oxo-4-hydroxyquinoline-3-carboxylic acid (**1a**) (2.33 g, 0.01 mol) was maintained on a metal bath at 250°C for 15 min, then cooled, washed with alcohol, and dried. Yield 1.62 g (98%); mp > 360°C (DMF). ^{1}H NMR spectrum: 11.54 (2H, s, NH); 8.46 (2H, d, 1,13-H); 7.83 (2H, t, 3, 11-H); 7.63 (2H, d, 4, 10-H); 7.37 ppm (2H, t, 2,12-H). Mass spectrum, *m/z* (I_{rel}, %): 330 (32) $[M]^+$, 302 (44), 274 (10), 44 (56), 39 (100). Found, %: C 69.21; H 3.10; N 8.34. $C_{19}H_{10}N_2O_4$. Calculated, %: C 69.09; H 3.05; N 8.48.

5,9-Dimethyl-6,7,8-trioxodiquinolino[3,4-*b*; 3',4'-*e*]-4H-pyran (2b) was obtained similarly. Yield 96%; mp > 360°C (DMF). ^{1}H NMR spectrum: 8.48 (2H, d, 1,13-H); 7.84 (2H, t, 3,11-H); 7.66 (2H, d, 4,10-H); 7.41 (2H, t, 2,12-H); 3.58 ppm (6H, s, Me). Mass spectrum: 358 (36) $[M]^+$, 329 (100). Found, %: C 70.28; H 3.99; N 7.84. $C_{21}H_{14}N_2O_4$. Calculated, %: C 70.39; H 3.94; N 7.82.

5,9-Diethyl-6,7,8-trioxodiquinolino[3,4-*b*;3',4'-*e*]-4H-pyran (2c) was obtained similarly. Yield 94%; mp > 360°C (DMF). ^{1}H NMR spectrum: 8.48 (2H, d, 1,13-H); 7.86 (2H, t, 3,11-H); 7.65 (2H, d, 4,10-H); 7.44 (2H, t, 2,12-H); 4.29 (4H, q, NCH_2); 1.29 ppm (6H, t, Me). Mass spectrum: 386 (100) $[M]^+$, 357 (61), 343 (12), 315 (33). Found, %: C 71.43; H 4.67; N 7.29. $C_{23}H_{18}N_2O_4$. Calculated, %: C 71.49; H 4.70; N 7.25.

X-ray Diffraction Study. The crystal system of pyran **2c** is triclinic; at 20°C, a = 12.555(3), b = 12.617(3), c = 13.630(3) Å; α = 110.43(2)°, β = 95.82(2)°, γ = 114.32(2)°; V = 1766.1(7) Å^3; d_{calc} = 1.453 g/cm^3; space group P_1; Z = 4.

TABLE 3. Bond Angles (ω) in the Pyran **2c** Structure

Angle	ω, deg.	Angle	ω, deg.
$C_{(13)}$ $N_{(1)}$ $C_{(14)}$	124.1(2)	$C_{(13)}$–$N_{(1)}$ $C_{(22)}$	118.9(2)
$C_{(14)}$ $N_{(1)}$–$C_{(22)}$	117.0(2)	$C_{(19)}$ $N_{(2)}$–$C_{(18)}$	123.8(2)
$C_{(19)}$–$N_{(2)}$–$C_{(20)}$	119.7(2)	$C_{(18)}$–$N_{(2)}$ $C_{(20)}$	116.5(2)
$C_{(6)}$ $O_{(1)}$ $C_{(7)}$	119.7(2)	$C_{(2)}$–$C_{(1)}$ $C_{(19)}$	120.5(2)
$C_{(1)}$–$C_{(2)}$ $C_{(3)}$	121.2(2)	$C_{(3)}$ $C_{(3)}$ $C_{(2)}$	119.4(2)
$C_{(3)}$–$C_{(4)}$ $C_{(5)}$	120.7(2)	$C_{(4)}$–$C_{(5)}$–$C_{(19)}$	119.9(2)
$C_{(4)}$–$C_{(5)}$ $C_{(6)}$	122.9(2)	$C_{(19)}$–$C_{(5)}$ $C_{(6)}$	117.1(2)
$C_{(17)}$–$C_{(6)}$ $O_{(1)}$	123.2(2)	$C_{(17)}$–$C_{(6)}$–$C_{(5)}$	123.8(2)
$O_{(1)}$ $C_{(6)}$–$C_{(5)}$	113.0(2)	$O_{(1)}$–$C_{(7)}$–$C_{(15)}$	122.2(2)
$O_{(1)}$ $C_{(7)}$–$C_{(8)}$	113.7(2)	$C_{(15)}$–$C_{(7)}$ $C_{(8)}$	124.2(2)
$C_{(13)}$–$C_{(8)}$–$C_{(9)}$	119.6(2)	$C_{(13)}$–$C_{(8)}$–$C_{(7)}$	117.4(2)
$C_{(9)}$–$C_{(8)}$–$C_{(7)}$	123.0(2)	$C_{(10)}$–$C_{(9)}$–$C_{(8)}$	120.5(2)
$C_{(9)}$–$C_{(10)}$ $C_{(11)}$	119.9(2)	$C_{(12)}$ $C_{(11)}$ $C_{(10)}$	121.3(2)
$C_{(11)}$ $C_{(12)}$ $C_{(13)}$	120.0(2)	$N_{(1)}$–$C_{(13)}$ $C_{(12)}$	122.0(2)
$N_{(1)}$ $C_{(13)}$ $C_{(8)}$	119.3(2)	$C_{(12)}$–$C_{(13)}$ $C_{(8)}$	118.7(2)
$O_{(2)}$–$C_{(14)}$–$N_{(1)}$	120.1(2)	$O_{(2)}$–$C_{(14)}$–$C_{(15)}$	123.4(2)
$N_{(1)}$–$C_{(14)}$–$C_{(15)}$	116.4(2)	$C_{(7)}$–$C_{(15)}$–$C_{(14)}$	118.3(2)
$C_{(7)}$ $C_{(15)}$–$C_{(16)}$	120.2(2)	$C_{(14)}$–$C_{(15)}$–$C_{(16)}$	121.5(2)
$O_{(3)}$–$C_{(16)}$–$C_{(15)}$	123.2(2)	$O_{(3)}$–$C_{(16)}$ $C_{(17)}$	122.7(2)
$C_{(15)}$–$C_{(16)}$–$C_{(17)}$	114.1(2)	$C_{(6)}$–$C_{(17)}$ $C_{(16)}$	119.0(2)
$C_{(6)}$ $C_{(17)}$ $C_{(16)}$	120.0(2)	$C_{(18)}$–$C_{(17)}$ $C_{(16)}$	121.1(2)
$O_{(4)}$–$C_{(18)}$ $N_{(2)}$	120.0(2)	$O_{(4)}$ $C_{(18)}$ $C_{(17)}$	123.7(2)
$N_{(2)}$–$C_{(18)}$–$C_{(17)}$	116.3(2)	$N_{(2)}$–$C_{(19)}$–$C_{(1)}$	122.1(2)
$N_{(2)}$–$C_{(19)}$ $C_{(5)}$	119.7(2)	$C_{(1)}$ $C_{(19)}$–$C_{(5)}$	118.2(2)
$N_{(2)}$ $C_{(20)}$–$C_{(21)}$	112.8(2)	$N_{(1)}$–$C_{(22)}$–$C_{(23)}$	111.9(2)
$C_{(13)}$ $N_{(1)}$ $C_{(14)}$	123.6(2)	$C_{(13)}$–$N_{(1)}$–$C_{(22)}$	120.2(2)
$C_{(14)}$–$N_{(1)}$–$C_{(22)}$	116.2(2)	$C_{(19)}$–$N_{(2)}$–$C_{(18)}$	123.8(2)
$C_{(19)}$ $N_{(2)}$ $C_{(20)}$	120.4(2)	$C_{(18)}$ $N_{(2)}$–$C_{(20)}$	115.8(2)
$C_{(7)}$ $O_{(1)}$–$C_{(6)}$	119.5(2)	$C_{(2)}$ $C_{(1)}$ $C_{(19)}$	120.5(2)
$C_{(1)}$–$C_{(2)}$ $C_{(3)}$	121.7(2)	$C_{(4)}$–$C_{(3)}$ $C_{(2)}$	119.5(2)
$C_{(3)}$–$C_{(4)}$ $C_{(5)}$	120.4(2)	$C_{(4)}$ $C_{(5)}$ $C_{(19)}$	120.1(2)
$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	123.0(2)	$C_{(19)}$ $C_{(5)}$ $C_{(6)}$	116.9(2)
$C_{(17)}$ $C_{(6)}$ $O_{(1)}$	122.2(2)	$C_{(17)}$ $C_{(6)}$ $C_{(5)}$	124.0(2)
$O_{(1)}$ $C_{(6)}$ $C_{(5)}$	113.8(2)	$C_{(15)}$ $C_{(7)}$–$O_{(1)}$	122.3(2)
$C_{(15)}$–$C_{(7)}$ $C_{(8)}$	124.1(2)	$O_{(1)}$ $C_{(7)}$–$C_{(8)}$	113.7(2)
$C_{(9)}$ $C_{(8)}$ $C_{(13)}$	120.2(2)	$C_{(9)}$–$C_{(8)}$ $C_{(7)}$	123.0(2)
$C_{(13)}$ $C_{(8)}$ $C_{(7)}$	116.9(2)	$C_{(10)}$–$C_{(9)}$–$C_{(8)}$	120.3(2)
$C_{(9)}$ $C_{(10)}$–$C_{(11)}$	119.5(2)	$C_{(12)}$ $C_{(11)}$–$C_{(10)}$	121.4(2)
$C_{(11)}$ $C_{(12)}$–$C_{(13)}$	120.5(2)	$N_{(1)}$ $C_{(13)}$ $C_{(12)}$	121.9(2)
$N_{(1)}$–$C_{(13)}$ $C_{(8)}$	119.9(2)	$C_{(12)}$ $C_{(13)}$ $C_{(8)}$	118.2(2)
$O_{(2)}$–$C_{(14)}$–$N_{(1)}$	120.1(2)	$O_{(2)}$–$C_{(14)}$–$C_{(15)}$	123.3(2)
$N_{(1)}$ $C_{(14)}$–$C_{(15)}$	116.7(2)	$C_{(7)}$–$C_{(15)}$ $C_{(14)}$	118.8(2)
$C_{(7)}$ $C_{(15)}$–$C_{(16)}$	120.3(2)	$C_{(14)}$ $C_{(15)}$ $C_{(16)}$	120.8(2)
$O_{(3)}$ $C_{(16)}$–$C_{(15)}$	123.7(2)	$O_{(3)}$ $C_{(16)}$ $C_{(17)}$	123.0(2)
$C_{(15)}$–$C_{(16)}$–$C_{(17)}$	113.3(2)	$C_{(6)}$–$C_{(17)}$–$C_{(16)}$	118.9(2)
$C_{(6)}$–$C_{(17)}$–$C_{(16)}$	120.3(2)	$C_{(18)}$–$C_{(17)}$ $C_{(16)}$	120.8(2)
$O_{(4)}$ $C_{(18)}$ $N_{(2)}$	119.9(2)	$O_{(4)}$ $C_{(18)}$–$C_{(17)}$	123.8(2)
$N_{(2)}$–$C_{(18)}$ $C_{(17)}$	116.2(2)	$N_{(2)}$–$C_{(19)}$ $C_{(1)}$	122.4(2)
$N_{(2)}$–$C_{(19)}$–$C_{(5)}$	119.7(2)	$C_{(1)}$ $C_{(19)}$–$C_{(5)}$	117.9(2)
$N_{(2)}$–$C_{(20)}$–$C_{(21)}$	110.9(2)	$N_{(1)}$–$C_{(22)}$–$C_{(23)}$	112.2(2)

The unit cell parameters and the intensities of 5960 independent reflections (R_{int} = 0.03) were measured on a Siemens P3/PC automatic diffractometer (λMoKα, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 50°). The structure was deciphered by the direct method using the SHELXTL PLUS program package [10]. The positions of the hydrogen atoms were calculated geometrically and refined using the "rider" model with fixed $U_{iso} = nU_{eq}$ for the nonhydrogen atom bonded to the given hydrogen atom (n = 1.5 for methyl groups and 1.2 for the remaining

hydrogen atoms). F^2 full-matrix least-squares refinement in the anisotropic approximation for the non-hydrogen atoms was done down to $wR_2 = 0.128$ ($R_1 = 0.051$ using 4198 reflections with $F > 4\sigma(F)$, $S = 1.07$).

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