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4-HYDROXY-2-QUINOLONES

119*. REACTION OF ETHYL 1-R-4-CHLORO-2-OXO-1,2-DIHYDROQUINOLINE-3-CARBOXYLATE WITH MALONONITRILE

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In acid medium ethyl 1-R-4-dicyanomethyl-2-oxo-1,2-dihydroquinoline-3-carboxylates are hydrated in the ketenimine tautomer form exclusively to the corresponding quinolylcyanoacetamides.

Keywords: malononitrile, 4-chloro-3-ethoxycarbonylquinolin-2-one, cyanoacetamide, hydrolysis, X-ray analysis.

In the presence of base many halo-substituted azaheterocycles can selectively exchange a halogen atom for a malononitrile residue to give the corresponding hetarylmalonodinitriles [2]. Depending on various factors (principally the structure of the starting hetaryl halide) such reactions sometimes give an unexpected result. Hence the reaction of ethyl 1-R-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylates (**1**) with the malononitrile carbanion and subsequent acidification of the reaction mixture with aqueous hydrochloric acid gave quinolylcyanoacetamides **2** rather than the expected quinolylmalononitriles [3]. The first stage of this reaction is undoubtedly the nucleophilic substitution of the chlorine atom in the chloroquinolines **1** by malononitrile. However, the question of at which step one of the nitrile groups is hydrolyzed to an amide and whether this process might be accompanied by more extensive hydrolysis to a substituted cyanoacetic acid remains unresolved. We have attempted to answer the problem in this communication.

In order to prevent any kind of "unexpectedness" in the synthesis we have used chromatographically pure reagents. The reaction was initially carried out as reported in method [3] both in ordinary and in anhydrous DMF.

However further inorganic material (excess K_2CO_3 and the KCl formed) was removed by precipitation with acetone and filtered. Removal of solvent from the filtrate gave the same 1-R-4-dicyanomethyl-3-ethoxycarbonyl-2-oxo-1,2-dihydroquinoline potassium salts **3** in both cases. Their structure was confirmed from their ^{1}H NMR spectra and , in the case of the N-ethyl derivative **3a** by X-ray analysis. The latter showed that, in the crystal, this compound exists as a 3D coordinated polymer in which the potassium atoms form a zigzag chain. Each of the two potassium atoms in the chain is bound alternately by two bridging $O_{(2)}$ atoms

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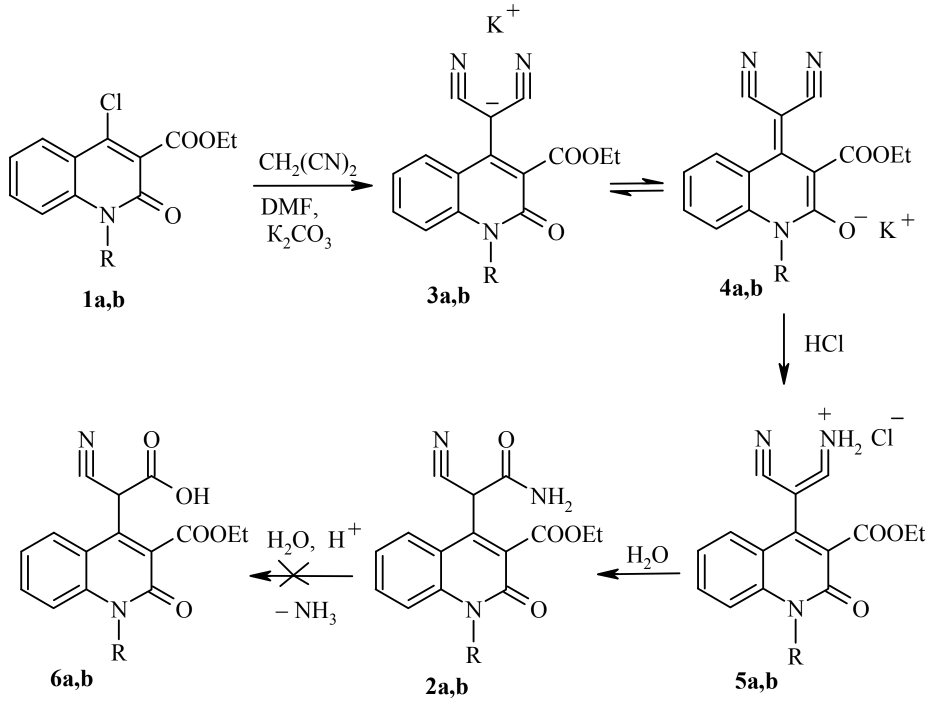
belonging to the two molecules as ligands **A** and **B** (Fig. 1) and two $O_{(1)}$ atoms, one of which is assigned to ligand **A** and the second to a third organic anion **C**. Additionally, each potassium atom is coordinated to the two atoms $N_{(2)}$ and $N_{(3)}$ of the cyano groups, one of which is assigned to ligand **B** and the second to a fourth ligand **D**. Hence each potassium atom is bound by six coordinated bonds with four molecules of organic ligand (Fig. 2). In turn, each organic anion is coordinated with four potassium cations (Fig. 3). The coordination sphere of the potassium atom is a strongly distorted octahedron (valence angles N–K–O, O–K–O, and N–K–N vary in the range 65.8-153.5º). The $O_{(1)}$ and $O_{(2)}$ atoms of ligand **A** and $O_{(2)}$ and $N_{(3)}$ atoms of ligand **B** lie in the basic octahedron. The potassium atom is coordinated with the $O_{(1)}$ atoms of ligand **C** and $N_{(2)}$ of ligand **D** in axial directions.



1–4 a R = Et, **b** R = Pr

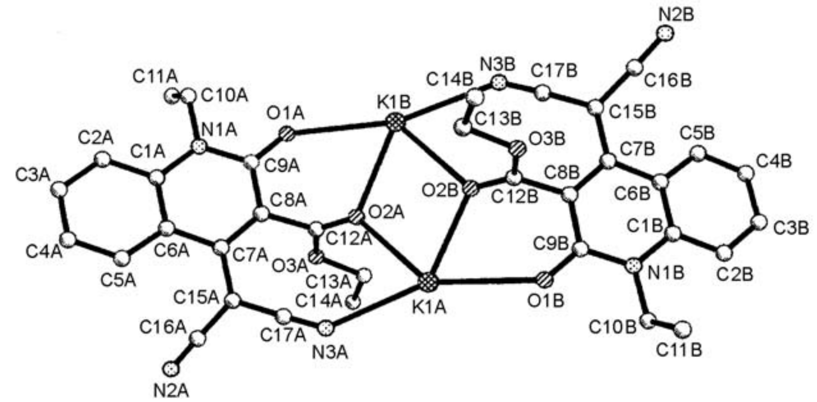


Fig. 1. Independent part of the unit cell with atomic numbering in the structure of the potassium salt **3a.**

Two potassium cations and two organic anions **A** and **B** are found in the independent part of the unit cell (Fig. 1). The bicyclic fragment of the organic anion is planar within 0.02 Å. The lengthening of the $O_{(1)}$–$C_{(9)}$ bond [1.248(2) in molecule **A**, 1.249(2) Å in molecule **B**] and $C_{(7)}$–$C_{(8)}$ [1.388(2) in **A** and 1.386(2) Å in **B**] when compared with their mean values of 1.210 and 1.332 Å respectively [4] with simultaneous shortening of the $C_{(7)}$–$C_{(15)}$ [1.448(2) in **A**, 1.452(2) Å in **B**] and $C_{(8)}$–$C_{(9)}$ bonds [1.436(2) in **A** and 1.437 (2) Å in **B**] (mean values 1.510 and 1.455 Å respectively) together with the fact that atoms $C_{(7)}$, $C_{(15)}$, $C_{(16)}$, and $C_{(17)}$ lie in a single plane allow us to establish the structure of the anion of the investigated salt as a resonance hybrid of two canonical structures **3** and **4** with a predominant contribution from the 1,2-dihydro form **3**.

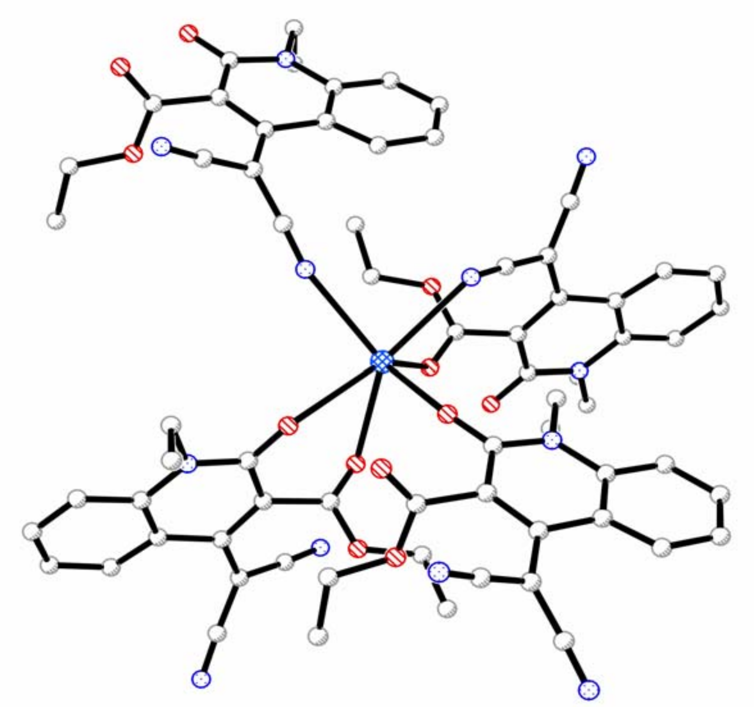


Fig. 2. Coordination sphere for the potassium atom in salt **3a.**

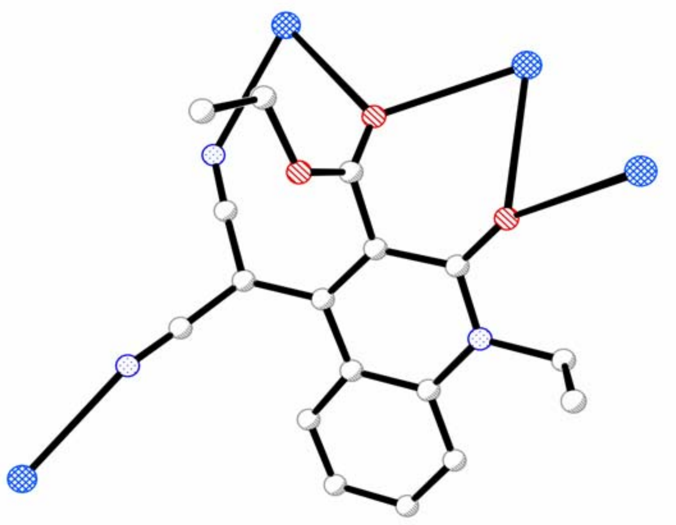


Fig. 3. Organic anion of salt **3a** coordinated by four potassium cations.

The ethyl substituent on atom $N_{(1)}$ is placed perpendicularly to the plane of the quinolone fragment [torsional angles $C_{(9)}$–$N_{(1)}$–$C_{(10)}$–$C_{(11)}$ 98.7(2)° in **A** and -99.3(2)° in **B**]. Repulsion between the ethyl group hydrogen atoms and the bicycle atoms [shortening of the intramolecular contacts $H_{(10a)}\cdots C_{(2)}$ 2.58 in **A** and 2.60 in **B** (sum of van der Waal radii 2.87 [5]); $H_{(10a)}\cdots H_{(2)}$ 2.03 in **A** and 2.07 in **B** (2.34); $H_{(10b)}\cdots O_{(1)}$ 2.31 in **A** and 2.27 Å in **B** (2.46 Å)] evidently determines the lengthening of the $N_{(1)}$–$C_{(9)}$ (1.383(2) in **A** and 1.379(2) in **B**) and $N_{(1)}$–$C_{(1)}$ bonds (1.401(2) Å in **A** and **B**) when compared with their mean values of 1.347 and 1.371 Å respectively.

Repulsion between the sterically close substituents on atoms $C_{(7)}$ and $C_{(8)}$ atoms [shortened contacts $N_{(3)}\cdots C_{(12)}$ 3.13 in **A** and 3.11 Å in **B** (3.21 Å)] leads to turning of both substituents relative to the plane of the bicyclic fragment [torsional angles $C_{(9)}$–$C_{(8)}$–$C_{(12)}$–$O_{(2)}$ 68.5(3) in **A** and -72.4(3)° in **B**; $C_{(8)}$–$C_{(7)}$–$C_{(15)}$–$C_{(17)}$ 29.3(3) in **A** and -28.9(3)° in **B**]. The ethyl group of the ester substituent is found in an ap conformation relative to the $C_{(12)}$–$C_{(8)}$ and $C_{(12)}$–$O_{(3)}$ bonds [torsional angles $C_{(13)}$–$O_{(3)}$–$C_{(12)}$–$C_{(8)}$ -177.3(2) in **A** and 177.8(2)° in **B**; $C_{(12)}$–$O_{(3)}$–$C_{(13)}$–$C_{(14)}$ -179.6(2) in **A** and 174.6(2)° in **B**]. A shortened $H_{(10c)}\cdots C_{(4a)}$ intermolecular contact (x-1, y, z) of 2.82 Å is found in the crystal.

Hence our investigation allows us to exclude unambiguously the possibility of hydration of the nitrile group to an amide in the initial stage of the synthesis.

Nitriles are stable to compound hydrolysis. As a rule their conversion to amides needs quite strong acid or base conditions. With the acidification of aqueous solutions of the potassium salts **3** addition of water occurs remarkable readily. This fact is in full agreement with our proposal that the initially formed

TABLE 1. Bond Lengths (l) in the Structure of the Potassium Salt **3a**

Bond	*l*, Å	Bond	*l*, Å
$K_{(1A)}$–$O_{(2B)}$	2.658(1)	$K_{(1A)}$–$N_{(3A)}$	2.799(2)
$K_{(1A)}$–$O_{(2A)}$	2.855(2)	$K_{(1A)}$–$O_{(1B)}$	2.901(1)
$N_{(1A)}$–$C_{(9A)}$	1.383(2)	$N_{(1A)}$–$C_{(1A)}$	1.401(2)
$N_{(1A)}$–$C_{(10A)}$	1.469(2)	$N_{(2A)}$–$C_{(16A)}$	1.149(2)
$N_{(3A)}$–$C_{(17A)}$	1.149(2)	$O_{(1A)}$–$C_{(9A)}$	1.248(2)
$O_{(2A)}$–$C_{(12A)}$	1.210(2)	$O_{(3A)}$–$C_{(12A)}$	1.324(2)
$O_{(3A)}$–$C_{(13A)}$	1.457(2)	$C_{(1A)}$–$C_{(2A)}$	1.408(3)
$C_{(1A)}$–$C_{(6A)}$	1.414(3)	$C_{(2A)}$–$C_{(3A)}$	1.373(3)
$C_{(3A)}$–$C_{(4A)}$	1.384(3)	$C_{(4A)}$–$C_{(5A)}$	1.374(3)
$C_{(5A)}$–$C_{(6A)}$	1.407(3)	$C_{(6A)}$–$C_{(7A)}$	1.453(2)
$C_{(7A)}$–$C_{(8A)}$	1.388(2)	$C_{(7A)}$–$C_{(15A)}$	1.448(2)
$C_{(8A)}$–$C_{(9A)}$	1.436(2)	$C_{(8A)}$–$C_{(12A)}$	1.499(2)
$C_{(10A)}$–$C_{(11A)}$	1.497(4)	$C_{(13A)}$–$C_{(14A)}$	1.479(4)
$C_{(15A)}$–$C_{(17A)}$	1.409(3)	$C_{(15A)}$–$C_{(16A)}$	1.411(2)
$K_{(1B)}$–$N_{(3B)}$	2.821(2)	$K_{(1B)}$–$O_{(2B)}$	2.929(2)
$N_{(1B)}$–$C_{(9B)}$	1.379(2)	$N_{(1B)}$–$C_{(1B)}$	1.401(2)
$N_{(1B)}$–$C_{(10B)}$	1.472(2)	$N_{(2B)}$–$C_{(16B)}$	1.148(2)
$N_{(3B)}$–$C_{(17B)}$	1.150(2)	$O_{(1B)}$–$C_{(9B)}$	1.249(2)
$O_{(2B)}$–$C_{(12B)}$	1.212(2)	$O_{(3B)}$–$C_{(12B)}$	1.320(2)
$O_{(3B)}$–$C_{(13B)}$	1.458(3)	$C_{(1B)}$–$C_{(2B)}$	1.405(3)
$C_{(1B)}$–$C_{(6B)}$	1.412(3)	$C_{(2B)}$–$C_{(3B)}$	1.376(3)
$C_{(3B)}$–$C_{(4B)}$	1.379(3)	$C_{(4B)}$–$C_{(5B)}$	1.377(3)
$C_{(5B)}$–$C_{(6B)}$	1.410(3)	$C_{(6B)}$–$C_{(7B)}$	1.456(2)
$C_{(7B)}$–$C_{(8B)}$	1.386(2)	$C_{(7B)}$–$C_{(15B)}$	1.452(2)
$C_{(8B)}$–$C_{(9B)}$	1.437(2)	$C_{(8B)}$–$C_{(12B)}$	1.497(2)
$C_{(10B)}$–$C_{(11B)}$	1.504(4)	$C_{(13B)}$–$C_{(14B)}$	1.492(5)
$C_{(15B)}$–$C_{(17B)}$	1.406(3)	$C_{(15B)}$–$C_{(16B)}$	1.413(2)

quinolylmalononitriles are hydrolyzed in the ketenimine tautomer form [3]. None the less it is known that the reaction of ketenimines with water to carboxamides occurs slowly [6] hence it can be more accurately said that the highly reactive keteniminium salts **5** undergoes rapid hydration since the synthesis occurs in acid medium.

In the chemistry of nitriles the ability of the amides formed to hydrolyze to acids more rapidly than the first stage of hydration to the amide is well known. Hence conversion of nitriles to amides without their subsequent hydrolysis to acids must occur under special conditions (in concentrated sulphuric or polyphosphoric acid, treatment with boron trifluoride in acetic acid etc.) [6].In the preparation of the cyanoacetamides **2** no special techniques are needed. Chromatographic monitoring shows that the basic material was present in the unpurified compounds **2a,b** at 98.7 and 99.1% respectively while traces of the theoretically possible quinolylcyanoacetic acids **6** as admixture were not found.

TABLE 2. Valence Angles (ω) in the Structure of the Potassium Salt **3a**

Angle	ω, deg	Angle	ω, deg
$O_{(2B)}–K_{(1A)}–N_{(3A)}$	138.60(5)	$N_{(3A)}–K_{(1A)}–O_{(2A)}$	69.67(5)
$C_{(9A)}–N_{(1A)}–C_{(1A)}$	122.1(2)	$C_{(9A)}–N_{(1A)}–C_{(10A)}$	117.7(2)
$C_{(1A)}–N_{(1A)}–C_{(10A)}$	120.2(2)	$C_{(17A)}–N_{(3A)}–K_{(1A)}$	138.0(2)
$C_{(12A)}–O_{(2A)}–K_{(1A)}$	126.7(1)	$C_{(12A)}–O_{(3A)}–C_{(13A)}$	118.1(2)
$N_{(1A)}–C_{(1A)}–C_{(2A)}$	120.7(2)	$N_{(1A)}–C_{(1A)}–C_{(6A)}$	120.2(2)
$C_{(2A)}–C_{(1A)}–C_{(6A)}$	119.1(2)	$C_{(3A)}–C_{(2A)}–C_{(1A)}$	120.8(2)
$C_{(2A)}–C_{(3A)}–C_{(4A)}$	120.7(2)	$C_{(5A)}–C_{(4A)}–C_{(3A)}$	119.3(2)
$C_{(4A)}–C_{(5A)}–C_{(6A)}$	122.1(2)	$C_{(5A)}–C_{(6A)}–C_{(1A)}$	117.9(2)
$C_{(5A)}–C_{(6A)}–C_{(7A)}$	122.8(2)	$C_{(1A)}–C_{(6A)}–C_{(7A)}$	119.3(2)
$C_{(8A)}–C_{(7A)}–C_{(15A)}$	122.1(2)	$C_{(8A)}–C_{(7A)}–C_{(6A)}$	117.4(2)
$C_{(15A)}–C_{(7A)}–C_{(6A)}$	120.5(2)	$C_{(7A)}–C_{(8A)}–C_{(9A)}$	123.3(2)
$C_{(7A)}–C_{(8A)}–C_{(12A)}$	122.3(2)	$C_{(9A)}–C_{(8A)}–C_{(12A)}$	114.0(2)
$O_{(1A)}–C_{(9A)}–N_{(1A)}$	120.4(2)	$O_{(1A)}–C_{(9A)}–C_{(8A)}$	122.2(2)
$N_{(1A)}–C_{(9A)}–C_{(8A)}$	117.2(2)	$N_{(1A)}–C_{(10A)}–C_{(11A)}$	112.0(2)
$O_{(2A)}–C_{(12A)}–O_{(3A)}$	123.3(2)	$O_{(2A)}–C_{(12A)}–C_{(8A)}$	125.8(2)
$O_{(3A)}–C_{(12A)}–C_{(8A)}$	110.9(1)	$O_{(3A)}–C_{(13A)}–C_{(14A)}$	107.7(2)
$C_{(17A)}–C_{(15A)}–C_{(16A)}$	116.1(2)	$C_{(17A)}–C_{(15A)}–C_{(7A)}$	120.2(2)
$C_{(16A)}–C_{(15A)}–C_{(7A)}$	123.2(2)	$N_{(2A)}–C_{(16A)}–C_{(15A)}$	177.7(2)
$N_{(3A)}–C_{(17A)}–C_{(15A)}$	177.5(2)	$N_{(3B)}–K_{(1B)}–O_{(2B)}$	66.33(5)
$C_{(9B)}–N_{(1B)}–C_{(1B)}$	122.2(2)	$C_{(9B)}–N_{(1B)}–C_{(10B)}$	117.9(2)
$C_{(1B)}–N_{(1B)}–C_{(10B)}$	119.9(2)	$C_{(17B)}–N_{(3B)}–K_{(1B)}$	141.6(2)
$C_{(12B)}–O_{(2B)}–K_{(1B)}$	128.9(1)	$C_{(12B)}–O_{(3B)}–C_{(13B)}$	116.5(2)
$N_{(1B)}–C_{(1B)}–C_{(2B)}$	120.8(2)	$N_{(1B)}–C_{(1B)}–C_{(6B)}$	120.0(2)
$C_{(2B)}–C_{(1B)}–C_{(6B)}$	119.2(2)	$C_{(3B)}–C_{(2B)}–C_{(1B)}$	120.6(2)
$C_{(2B)}–C_{(3B)}–C_{(4B)}$	120.8(2)	$C_{(3B)}–C_{(4B)}–C_{(5B)}$	119.7(2)
$C_{(4B)}–C_{(5B)}–C_{(6B)}$	121.5(2)	$C_{(5B)}–C_{(6B)}–C_{(1B)}$	118.2(2)
$C_{(5B)}–C_{(6B)}–C_{(7B)}$	122.2(2)	$C_{(1B)}–C_{(6B)}–C_{(7B)}$	119.5(2)
$C_{(8B)}–C_{(7B)}–C_{(15B)}$	121.7(2)	$C_{(8B)}–C_{(7B)}–C_{(6B)}$	117.2(2)
$C_{(15B)}–C_{(7B)}–C_{(6B)}$	121.1(2)	$C_{(7B)}–C_{(8B)}–C_{(9B)}$	123.3(2)
$C_{(7B)}–C_{(8B)}–C_{(12B)}$	122.7(2)	$C_{(9B)}–C_{(8B)}–C_{(12B)}$	113.6(2)
$O_{(1B)}–C_{(9B)}–N_{(1B)}$	120.6(2)	$O_{(1B)}–C_{(9B)}–C_{(8B)}$	122.0(2)
$N_{(1B)}–C_{(9B)}–C_{(8B)}$	117.3(2)	$N_{(1B)}–C_{(10B)}–C_{(11B)}$	112.4(2)
$O_{(2B)}–C_{(12B)}–O_{(3B)}$	123.5(2)	$O_{(2B)}–C_{(12B)}–C_{(8B)}$	125.1(2)
$O_{(3B)}–C_{(12B)}–C_{(8B)}$	111.4(2)	$O_{(3B)}–C_{(13B)}–C_{(14B)}$	107.5(3)
$C_{(17B)}–C_{(15B)}–C_{(16B)}$	116.2(2)	$C_{(17B)}–C_{(15B)}–C_{(7B)}$	120.3(2)
$C_{(16B)}–C_{(15B)}–C_{(7B)}$	123.1(2)	$N_{(2B)}–C_{(16B)}–C_{(15B)}$	177.4(2)
$N_{(3B)}–C_{(17B)}–C_{(15B)}$	177.2(2)		

EXPERIMENTAL

^1H NMR spectra for the synthesized compounds were recorded on a Varian Mercury VX-200 (200 MHz) instrument using DMSO-d_6 solvent and TMS as internal standard. Chromato-mass spectra for the cyanoacetamides **2** were taken on an Agilent 1100 LC/MSD spectrometer using APCI ionization (atmospheric pressure chemical ionization). The chromatography conditions were: column length 50 mm diameter 4.6 mm, stationary phase Zorbax Eclipse XDB-C18, solvent aqueous acetonitrile acidified with 0.1% trifluoroacetic acid, gradient elution, solvent flow 2.4 ml/min.

4-Dicyanomethyl-3-ethoxycarbonyl-1-ethyl-2-oxo-1,2-dihydroquinoline Potassium Salt (3a). Malononitrile (0.72 g, 0.011 mol) and K_2CO_3 (2 g) were added to a solution of ethyl 4-chloro-1-ethyl-2-oxo-1,2-dihydroquinoline-3-carboxylate **1a** (2.79 g, 0.01 mol) in DMF (15 ml) and stirred for 3.5 h at 50ºC. After cooling, it was treated with acetone (50 ml) and filtered. The precipitate was washed on the filter several times with acetone. The solvent was removed from the filtrate *in vacuo*. The residue was again dissolved in acetone, filtered if necessary, and the compound was precipitated with hexane or ether. The yellow solid salt **3a** was filtered off, washed with hexane or ether, and dried. Yield 2.95 g (85%); mp 263-265ºC. Single crystals for X-ray analysis were obtained by crystallization from acetone. ^1H NMR spectrum, δ, ppm (*J*, Hz); 8.48 (1H, dd, *J* = 8.3 and 1.5, H-5); 7.54 (1H, td, *J* = 7.7 and 1.5, H-7); 7.42 (1H, dd, *J* = 8.6 and 1.1, H-8); 7.14 (1H, td, *J* = 7.5 and 1.4, H-6); 4.15 (4H, m, NCH_2 + OCH_2); 1.22 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$); 1.12 (3H, t, *J* = 7.1, $NCH_2C\underline{H}_3$). Found, %: C 58.89; H 4.15; N 12.17. $C_{17}H_{14}KN_3O_3$. Calculated, %: C 58.77; H 4.06;N 12.09.

4-Dicyanomethyl-3-ethoxycarbonyl-2-oxo-1-propyl-1,2-dihydroxyquinoline Potassium Salt (3b) was prepared similarly. Yield 3.28 g (91%); mp 247-249ºC. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.46 (1H, dd, *J* = 8.4 and 1.5, H-5); 7.53 (1H, td, *J* = 7.9 and 1.2, H-7); 7.41 (1H, dd, *J* = 8.6 and 1.0, H-8); 7.13 (1H, td, *J* = 7.4 and 1.3, H-6); 4.14 (2H, q, *J* = 7.0, OCH_2); 4.05 (2H, t, *J* = 8.1, NCH_2); 1.56 (2H, m, $NCH_2C\underline{H}_2$); 1.21 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$); 0.91 (3H, t, *J* = 7.5, $NCH_2CH_2C\underline{H}_3$). Found, %: C 59.94; H 4.60; N 11.56. $C_{18}H_{16}KN_3O_3$. Calculated, %: C 59.82; H 4.46; N 11.63.

Ethyl 4-(Carbamoylcyanomethyl)-1-ethyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (2a). A solution of the corresponding potassium salt **3a** (0.35 g, 0.001 mol) in water (5 ml) was acidified with HCl to pH 4 and left in an evaporating dish at room temperature to full dryness. For removal of KCl the residue was treated with dry acetone (5 ml) and filtered after several hours. The residue on the filter was washed with dry acetone after which the solvent was removed from the filtrate. Chromato-mass spectrometry was carried out initially on an unpurified and then a sample recrystallized from ethanol and these were compared with a known sample [3]. The content of the basic material in the sample increased from 98.70 to 99.96%. Mass spectrum, *m/z* (I_{rel}, %): 285 $[M-CONH_2+H]^+$ (97), 282 $[M-EtOH+H]^+$ (15), 213 $[M-CONH_2-COOC_2H_4+H]^+$ (100).

Ethyl 4-(Carbamoylcyanomethyl)-2-oxo-1-propyl-1,2-dihydroquinoline-3-carboxylate (2b) was prepared from the potassium salt **3b** and studied as in the preceding example. The content of the basic material in the impure compound was 99.12% and 99.94% after recrystallization from ethanol. Mass spectrum, *m/z* (I_{rel}, %): 299 $[M-CONH_2]^+$ (95), 296 $[M-EtOH+H]^+$ (17), 227 $[M-CONH_2-COOC_2H_4+H]^+$ (100).

In addition, the cyanoacetamides **2** were identified from their ^1H NMR spectrum and also by the absence of a melting point depression when mixed with a known sample [3].

X-Ray Analysis. Crystals of the potassium salt **3a** are monoclinic (acetone) at 20ºC: a = 13.926(1), b = 19.033(1), c = 14.118(1) Å, β = 118.47(1)º, V = 3289.6(3) Å^3, M_r = 347.41, Z = 8, space group $P2_1/n$, d_{calc} = 1.403 g/cm^3, μMoKα = 0.343 mm^{-1}, $F(000)$ = 1440. The unit cell parameters and intensities of 17612 reflections (7523 independent, R_{int} = 0.035) were measured on an Xcalibur-3 diffractometer (MoKα radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 55º).

The structure was solved by a direct method using the SHELXTL [7] program package. The position of the hydrogen atoms were revealed in electron density difference synthesis and refined isotropically. The structure was refined by F^2 full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms to $wR_2 = 0.112$ for 7495 reflections ($R_1 = 0.047$ for 5503 reflections with $F>4\sigma(F)$, $S = 1.046$). The full crystallographic information has been placed in the Cambridge structural data bank (reference CCDC 296936). Interatomic distances and valence angles are given in Tables 1 and 2.

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