Chemistry of Heterocyclic Compounds, Vol. 43, No. 5, 2007

4-HYDROXY-2-QUINOLONES. 114*. SYNTHESIS AND STRUCTURE OF 6-R-5-HYDROXY-2,4-DIOXO-2,3,4,6-TETRAHYDROBENZO-[*c*][2,7]NAPHTHYRIDINE-1-CARBONITRILES

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Hydration of ethyl 1-R-4-dicyanomethyl-2-oxo-1,2-dihydroquinoline-3-carboxylate gives the corresponding substituted cyanoacetamides which are readily and quantitatively cyclized to 6-R-5-hydroxy-2,4-dioxo-2,3,4,6-tetrahydrobenzo[c][2,7]naphthyridine-1-carbonitriles in the presence of aqueous base.

Keywords: benzonaphthyridine, 4-chloro-3-ethoxycarbonyl-2-quinolinone, malononitrile, cyanoacetamide, hydrolysis, X-ray analysis.

The basic hydrolysis of 1-R-4-(cyanocarbethoxymethyl)-3-ethoxycarbonyl-2-oxo-1,2-dihydroquinolines with simultaneous or subsequent decarboxylation is a preparatively convenient method for obtaining 4-methyl substituted 1-R-2-oxo-1,2-dihydroquinoline-3-carboxylic acids [2, 3]. The key stage in this synthesis which determines its efficiency overall is the exchange of the halogen atom in 1-R-4-chloro-3-ethoxycarbonyl-2-oxo-1,2-dihydroquinolines **1** for a cyanoacetate residue. Although these reactions proceed in good yields there is undoubtedly interest in the exchange of the cyanoacetate residue for other active methylene compounds. Hence the selectivity and high reactivity in reactions of malononitrile with many hetaryl halides are well known [4]. This situation has led to our investigation.

It was found that 4-chloroquinolines **1** react very vigorously with malononitrile in the system DMF-K_2CO_3 and the reaction occurs with marked heat evolution. It was thought that dilution of the reaction mixture with water and acidification would give the corresponding quinolinemalononitriles **2**. However, the ^{1}H NMR spectra of the compounds prepared showed signals for the protons of the benzene part of the molecule, the 4-CH, 3-COOEt, and 1-N-alkyl groups with typical multiplicities but also two "extra" singlets of intensity 1H each in the aromatic region which clearly did not correspond with the expected structure.

According to X-ray data it was possible to show that the samples obtained are not the malononitriles **2** but substituted cyanoacetamides **4** (Table 1). Hence the "extra" signals in the ^{1}H NMR spectra can be assigned as the magnetically nonequivalent protons of an amide group (Table 2). In the case of ethyl 4-(carbamoyl-cyanomethyl)-1-ethyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**4b**) it was found that the pyridone ring occurs in such compounds in a strongly flattened boat conformation (folding parameters: $S = 0.1$, $\theta = 84.2$, $\Psi = 3.6$ [5]). The deviations of atoms $C_{(7)}$ and $N_{(1)}$ from the mean square plane of the remaining ring atoms are -0.07 and

* For Communication 113 see [1].

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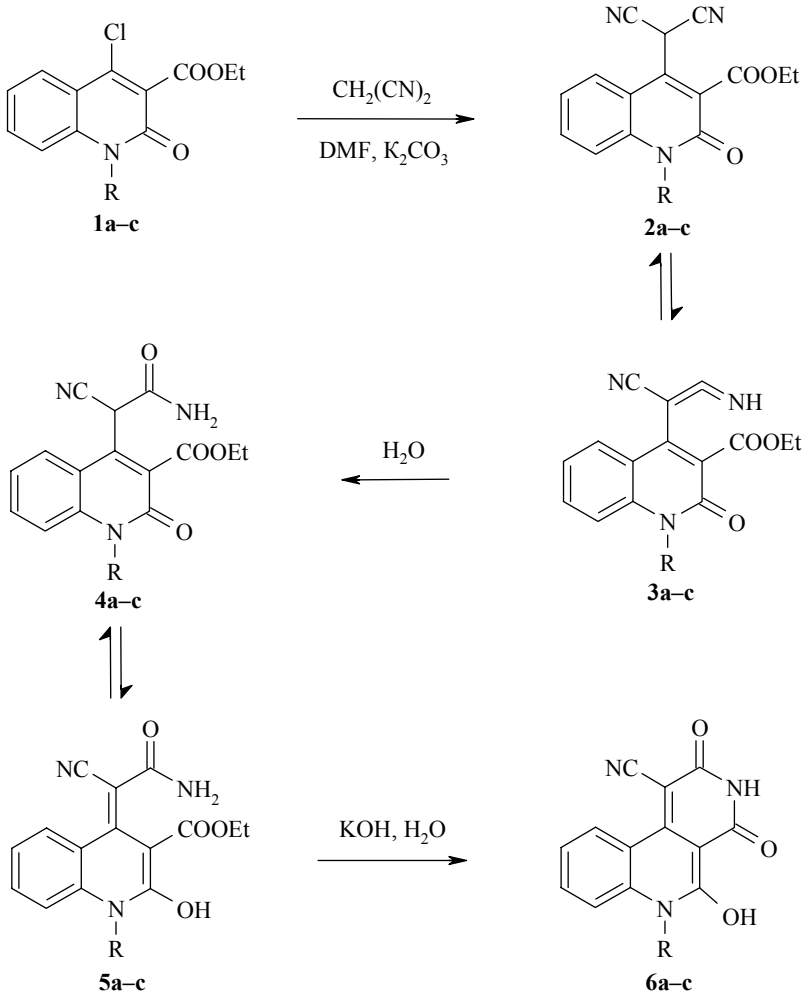


1–6 a R = Me, **b** R = Et, **c** R = Pr

TABLE 1. Parameters for the Cyanoacetamides 4 and Benzonaphthyridines **6**.

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
4a	$C_{16}H_{15}N_3O_4$	61.48 / 61.34	4.95 / 4.83	13.33 / 13.41	182 (dec.)	72
4b	$C_{17}H_{17}N_3O_4$	62.30 / 62.38	5.32 / 5.23	12.71 / 12.84	190 (dec.)	74
4c	$C_{18}H_{19}N_3O_4$	63.46 / 63.33	5.73 / 5.61	12.44 / 12.31	193 (dec.)	77
6a	$C_{14}H_9N_3O_3$	62.82 / 62.92	3.27 / 3.39	15.64 / 15.72	> 335	98
6b	$C_{15}H_{11}N_3O_3$	64.13 / 64.05	3.99 / 3.94	14.85 / 14.94	> 335	97
6c	$C_{16}H_{13}N_3O_3$	65.01 / 65.08	4.38 / 4.44	14.30 / 14.23	> 335	98

TABLE 2. Spectroscopic Parameters for the Compounds Synthesized*

Compound	^{1}H NMR spectrum δ, ppm. (*J*, Hz)
4a	7.86 (1H, dd, *J* = 8.0 and *J* = 1.2, H-5); 7.77 (1H, s, NH); 7.72 (1H, td, *J* = 7.7 and *J* = 1.3, H-7); 7.65 (1H, dd, *J* = 8.2 and *J* = 1.0, H-8); 7.39 (1H, td, *J* = 7.3 and *J* = 1.3, H-6); 7.29 (1H, s, NH); 5.60 (1H, s, 4-CH); 4.34 (2H, q, *J* = 7.1, OCH_2); 3.65 (3H, s, NCH_3); 1.27 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$)
4b	7.88 (1H, d, *J* = 8.1, H-5); 7.79 (1H, s, NH); 7.71-7.67 (2H, m, H-7,8); 7.39 (1H, td, *J* = 7.1 and *J* = 1.2, H-6); 7.31 (1H, s, NH); 5.59 (1H, s, 4-CH); 4.41-4.18 (4H, m, OCH_2 + NCH_2); 1.32-1.12 (6H, m, $OCH_2C\underline{H}_3$ + $NCH_2C\underline{H}_3$)
4c	7.85 (1H, d, *J* = 8.1, H-5); 7.77 (1H, s, NH); 7.73-7.66 (2H, m, H-7,8); 7.38 (1H, td, *J* = 7.0 and *J* = 1.1, H-6); 7.31 (1H, s, NH); 5.59 (1H, s, 4-CH); 4.34 (2H, q, *J* = 7.2, OCH_2); 4.19 (2H, t, *J* = 7.7, NCH_2); 1.63 (2H, m, $NCH_2C\underline{H}_2$); 1.28 (3H, t, *J* = 7.2, $OCH_2C\underline{H}_3$); 0.96 (3H, t, *J* = 7.3, $NCH_2CH_2C\underline{H}_3$)
6a	12.90 (1H, br. s, NH); 9.08 (1H, d, *J* = 8.1, H-10); 7.87-7.68 (2H, m, H-7,8); 7.43 (1H, t, *J* = 7.1, H-9); 3.53 (3H, s, CH_3)
6b	12.98 (1H, br. s, NH); 9.13 (1H, d, *J* = 8.2, H-10); 7.90-7.73 (2H, m, H-7,8); 7.48 (1H, t, *J* = 7.0, H-9); 4.31 (2H, q, *J* = 7.1, NCH_2); 1.26 (3H, t, *J* = 7.0, CH_3)
6c	12.93 (1H, br. s, NH); 9.12 (1H, d, *J* = 8.1, H-10); 7.88-7.70 (2H, m, H-7,8); 7.46 (1H, t, *J* = 7.1, H-9); 4.19 (2H, t, *J* = 7.5, NCH_2); 1.65 (2H, m, $NCH_2C\underline{H}_2$); 0.94 (3H, t, *J* = 7.4, CH_3);

* Mass spectrum, *m/z* (I_{rel}, %): **6a** 268 $[M+H]^+$ (12), 267 $[M]^+$ (100), 252 $[M-CH_3]^+$ (18), 179 (14), 127 (23), 76 (17); **6b** 282 $[M+H]^+$ (14), 281 $[M]^+$ (100), 266 $[M-CH_3]^+$ (22), 253 $[M-C_2H_4]^+$ (47), 179 (12), 149 (27), 127 (10), 76 (14); **6c** 296 $[M+H]^+$ (9), 295 $[M]^+$ (36), 266 $[M-C_2H_5]^+$ (22), 253 $[M-C_3H_6]^+$ (100), 225 (10), 179 (10), 170 (38), 165 (22), 153 (46), 127 (52).

-0.05 Å respectively (Fig. 1, Tables 3, 4). The non planarity of the heterocycle, the twist of the $C_{(7)}$ to $C_{(8)}$ double bond (torsional angle $C_{(6)}$–$C_{(7)}$–$C_{(8)}$–$C_{(9)}$ -6.0(2)º), and the lengthening of the $C_{(7)}$–$C_{(8)}$ 1.360(2) (mean value 1.326 [6]), $C_{(7)}$–$C_{(13)}$ 1.541(2) (1.510), $C_{(8)}$–$C_{(10)}$ 1.505(2) (1.488), and $C_{(13)}$–$C_{(14)}$ 1.556(2) (1.514) Å bonds are most likely due to the powerful repulsion between the spatially close substituents on atoms $C_{(7)}$ and $C_{(8)}$ and the hydrogen atoms of the aromatic ring [shortened intramolecular contacts $H_{(5)}$…$C_{(13)}$ 2.69 (sum of van der Waal radii 2.87 [7]), $H_{(5)}$…$C_{(14)}$ 2.36 (2.87), and $H_{(13)}$…$C_{(10)}$ 2.43 (2.87 Å)]. The ester substituent on $C_{(8)}$ is twisted relative to the endocyclic double bond (torsional angle $C_{(7)}$–$H_{(8)}$–$C_{(10)}$–$O_{(2)}$ 61.5(2)º) and the ethyl group is found in a +*sc* conformation relative to the $C_{(10)}$–$O_{(3)}$ bond (torsional angle $C_{(10)}$–$O_{(3)}$–$C_{(11)}$–$C_{(12)}$ 74.9(2)º). This orientation of the ester group is additionally stabilized by a weak intramolecular hydrogen bond C_{13}–$H_{(13)}$…$O_{(2)}$, H…O 2.27 Å C–H…O 137º. The nitrile group is almost perpendicular to the bicyclic fragment (torsional angle $C_{(8)}$–$C_{(7)}$–$C_{(13)}$–$C_{(15)}$ -92.2(2)º) and the acetamide group is found in a –*ac*-position relative to the $C_{(7)}$–$C_{(8)}$ bond but turned in such a way that the $O_{(4)}$ atom has a –*ac*-orientation relative to the $C_{(7)}$–$C_{(13)}$ bond (torsional angles $C_{(8)}$–$C_{(7)}$–$C_{(13)}$–$C_{(14)}$ -140.6(2)º, $C_{(7)}$–$C_{(13)}$–$C_{(14)}$–$O_{(4)}$ -122.7(2)º).

The ethyl group on atom $N_{1)}$ is positioned almost perpendicular to the plane of the bicycle (torsional angle $C_{(1)}$–$N_{(1)}$–$C_{(16)}$–$C_{(17)}$ 88.5(2)º and the bonds $N_{(1)}$–$C_{(9)}$ 1.373(2), $N_{(1)}$–$C_{(1)}$ 1.398(2), and $N_{(1)}$–$C_{(16)}$ 1.483(2) Å are somewhat shortened when compared with the mean values of 1.355, 1.371, and 1.469 Å respectively as a consequence of the repulsion between the substituent on $N_{(1)}$ and the neighboring carbonyl group and hydrogen atom in the *peri* position of the benzene ring [shortened intramolecular contacts $H_{(2)}$…$C_{(16)}$ 2.51 (2.87), $H_{(2)}$…$H_{(16b)}$ 2.12 (2.34), $H_{(16b)}$…C_2 2.61 (2.87), and $H_{(16a)}$…$O_{(1)}$ 2.32 (2.46 Å)].

In the crystal, the molecules of cyanoacetamide **4b** are stacked along the crystallographic (1 0 0) direction connected by the intermolecular bonds $N_{(3)}$–$H_{(3Na)}$…$O_{(1)}$ (-*x*, 1-*y*, 1-*z*), H…O 2.07 Å, N–H…O 159º; $N_{(3)}$–$H_{(3Nb)}$…$O_{(1)}$ (*x*-1, *y*, *z*), H…O 2.13 Å, N–H…O 151º. Shortening of the intermolecular contacts is also observed in the crystal $H_{(2)}$...$N_{(2)}$ (-*x*, 1-*y*, -*z*) 2.59(2.67) and $H_{(13)}$…$N_{2)}$ (-*x*, 2-*y*, 1-*z*) 2.58 (2.67 Å).

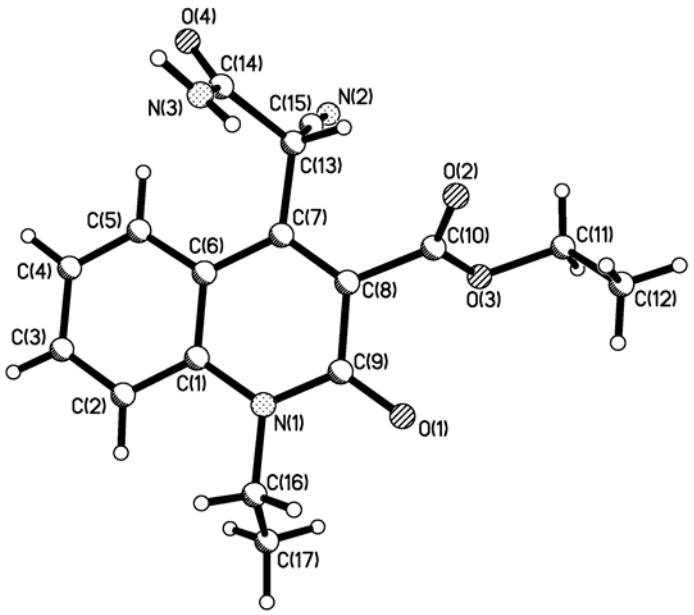


Fig. 1. Structure of the cyanoacetamide molecule **4b** with atomic numbering.

The ease of addition of a molecule of water observed and the fact that only one of the two cyano groups is hydrated allow us to propose that, like tricyanomethane (cyanoform) [8], the intermediate formed quinolinemalononitriles **2** exist as the ketenimine tautomeric form **3** which itself also reacts with water.

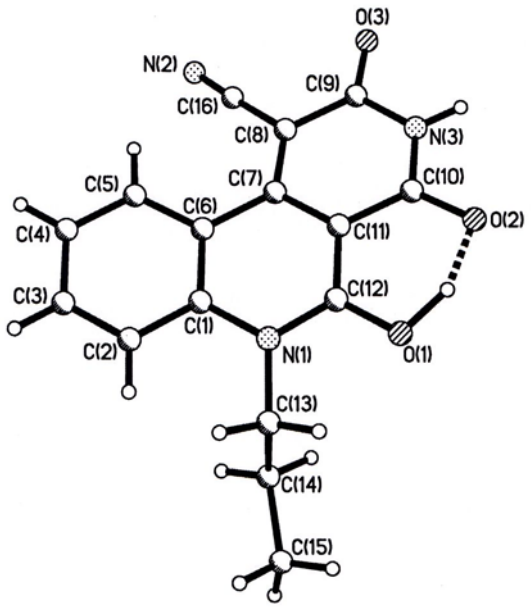
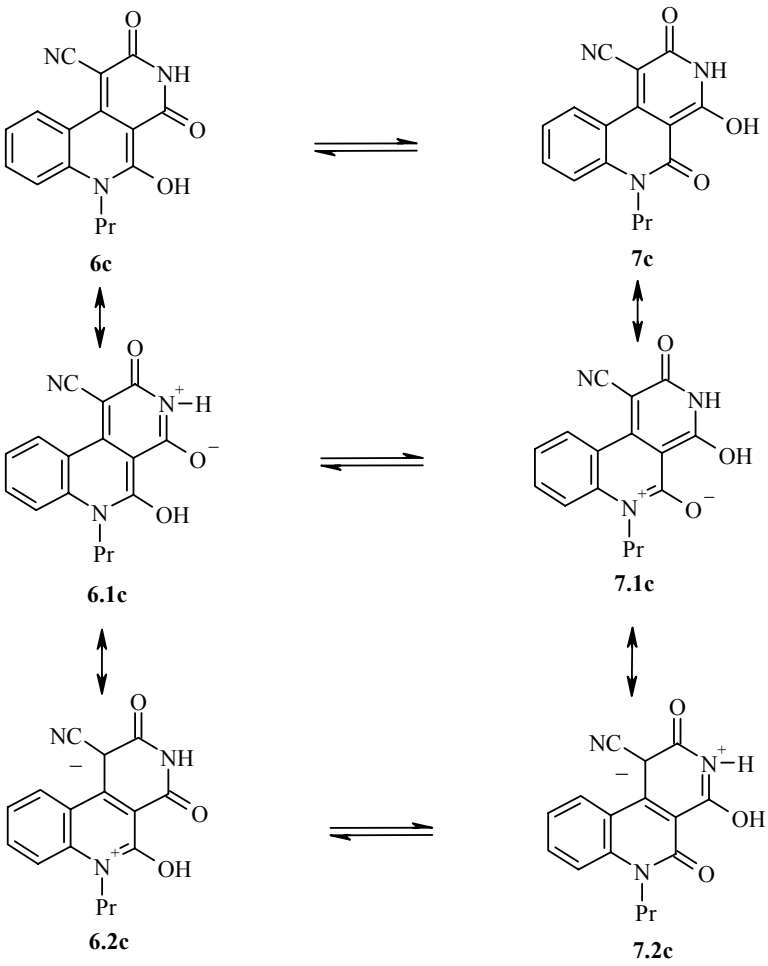


Fig. 2. Structure of the benzonaphthyridine molecule **6c** with atomic numbering.
The dashed line shows the intramolecular hydrogen bond.

Since amides are typical intermediate products in the hydrolysis of nitriles to carboxylic acids [9] the cyanoacetamides **4** can be considered (at least theoretically) as the first step in the reaction of dinitriles **2** to 1-R-4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acids. None the less, subsequent investigation shows that the practical realization of this transformation is not possible.

When separated in the pure state the cyanoacetamides **4** are colorless, crystalline materials. At the same time their solutions in aqueous bases have an intense yellow color, evidently *via* formation of the ylidene form **5**. When these solutions are heated to reflux the color immediately disappears and a colorless precipitate forms which does not then undergo any further change.

It follows from their NMR spectra that the ester and carbamide groups take part in this reaction. The strong (average of 1.25 ppm) low field shift of the H-5 proton signal of the quinolone ring can be viewed as the result of heterocyclization where the indicated proton proves to be in close proximity to the strongly magnetically anisotropic C≡N group. Due to free rotation, in the starting cyanoacetamides **4** such a close approach does not occur and the corresponding signal is shifted to higher field.



The mass spectra show a 46 atomic mass unit loss from the starting cyanoacetamides **4** which actually corresponds to the surprisingly ready closing of the dioxopyridine ring with loss of ethanol to form virtually quantitative yields of the 6-R-5-hydroxy-2,4-dioxo-2,3,4,6-tetrahydrobenzo[*c*][2,7]naphthyridine-1-carbonitriles **6** in the final stage.

TABLE 3. Bond Lengths (*l*) in the Cyanoacetamide **4b** and Benzonaphthyridine **6c** Structures

Bond	*l*, Å	Bond	*l*, Å
Cyanoacetamide **4b**		Benzonaphthyridine **6c**	
$O_{(1)}–C_{(9)}$	1.246(2)	$N_{(1)}–C_{(12)}$	1.345(3)
$O_{(3)}–C_{(10)}$	1.328(2)	$N_{(1)}–C_{(13)}$	1.489(3)
$O_{(4)}–C_{(14)}$	1.219(2)	$N_{(3)}–C_{(10)}$	1.344(3)
$N_{(1)}–C_{(1)}$	1.398(2)	$O_{(1)}–C_{(12)}$	1.299(3)
$N_{(2)}–C_{(15)}$	1.142(2)	$O_{(3)}–C_{(9)}$	1.239(3)
$C_{(1)}–C_{(2)}$	1.416(2)	$C_{(1)}–C_{(6)}$	1.418(3)
$C_{(2)}–C_{(3)}$	1.384(2)	$C_{(3)}–C_{(4)}$	1.399(3)
$C_{(4)}–C_{(5)}$	1.380(2)	$C_{(5)}–C_{(6)}$	1.405(3)
$C_{(6)}–C_{(7)}$	1.449(2)	$C_{(7)}–C_{(11)}$	1.405(3)
$C_{(7)}–C_{(13)}$	1.541(2)	$C_{(8)}–C_{(16)}$	1.428(3)
$C_{(8)}–C_{(10)}$	1.505(2)	$C_{(10)}–C_{(11)}$	1.429(3)
$C_{(13)}–C_{(15)}$	1.466(2)	$C_{(13)}–C_{(14)}$	1.525(3)
$C_{(16)}–C_{(17)}$	1.511(3)	$N_{(1)}–C_{(1)}$	1.412(3)
$O_{(2)}–C_{(10)}$	1.209(2)	$N_{(2)}–C_{(16)}$	1.158(3)
$O_{(3)}–C_{(11)}$	1.469(2)	$N_{(3)}–C_{(9)}$	1.390(3)
$N_{(1)}–C_{(9)}$	1.373(2)	$O_{(2)}–C_{(10)}$	1.282(3)
$N_{(1)}–C_{(16)}$	1.483(2)	$C_{(1)}–C_{(2)}$	1.398(3)
$N_{(3)}–C_{(14)}$	1.328(2)	$C_{(2)}–C_{(3)}$	1.369(3)
$C_{(1)}–C_{(6)}$	1.416(2)	$C_{(4)}–C_{(5)}$	1.379(3)
$C_{(3)}–C_{(4)}$	1.393(2)	$C_{(6)}–C_{(7)}$	1.472(3)
$C_{(5)}–C_{(6)}$	1.412(2)	$C_{(7)}–C_{(8)}$	1.405(3)
$C_{(7)}–C_{(8)}$	1.360(2)	$C_{(8)}–C_{(9)}$	1.445(3)
$C_{(8)}–C_{(9)}$	1.458(2)	$C_{(11)}–C_{(12)}$	1.425(3)
$C_{(11)}–C_{(12)}$	1.506(3)	$C_{(14)}–C_{(15)}$	1.531(3)
$C_{(13)}–C_{(14)}$	1.556(2)		

X-Ray diffraction of the 6-N-propyl derivative **6c** (Fig. 2, Tables 3, 4) also served to confirm this route for the reaction studied. It was shown that the pyridinedione fragment of the benzonaphthyridine **6c** is planar to within 0.01 Å. The hydroxypyridine ring occurs in a *chair* conformation. The deviation of atom $C_{(7)}$ from the mean plane of the remaining ring atoms is 0.11 Å. The non-planar conformation of the hydroxypyridine ring is likely due to the rather strong repulsion between the $C_{(8)}$ nitrile group and the benzene ring atoms [intramolecular contact shortening $H_{(5)}…C_{(8)}$ 2.80 (sum of van der Waal radii 2.87 [7]), $H_{(5)}…C_{(16)}$ 2.32 (2.87), $H_{(5)}…N_{(2)}$ 2.58 (2.67), $C_{(16)}…C_{(5)}$ 2.97 (3.42 Å)]. It should be noted that the cyano group is somewhat non linear ($N_{(2)}–C_{(16)}–C_{(8)}$valence angle 176.4(2)ºC).

The position of the $H_{(10)}$ hydroxy group hydrogen was revealed directly in electron density difference synthesis and refined in the isotropic approximation. This showed that the benzonaphthyridine **6c** exists principally as the 5-hydroxy tautomer. However, the similarity of the bond lengths $O_{(1)}–C_{(12)}$ 1.299(3) and $O_{(2)}–C_{(10)}$ 1.282(3) on the one hand and $C_{(11)}–C_{(12)}$ 1.425(3) and $C_{(11)}–C_{(10)}$ 1.429(3) Å on the other suggest that the investigated structure can be described as a superposition of the two tautomers **6c** and **7c**. This proposal also agrees with the presence of a very strong intramolecular hydrogen bond $O_{(1)}–H_{(10)}…O_{(2)}$ (H…O 1.38 Å, O–H…O 155º) suggesting a rather low barrier to the transfer of a proton between the oxygen atoms. In addition each tautomer can be described by three resonance structures. The contribution of resonance structures **6.1c** and **7.1c** are indicated by the shortening of the bond lengths $N_{(1)}–C_{(12)}$ 1.345(3) and $N_{(3)}–C_{(10)}$ 1.344 (3) when compared with their mean value of 1.385 Å [6]. The similarity of the bond lengths $C_{(7)}–C_{(8)}$ 1.405(3) (mean value 1.326) and $C_{(7)}–C_{(11)}$ 1.405(3) (1.455 Å) confirm the presence of the resonance structures **6.2c** and **7.2c**.

TABLE 4. Valence Angles (ω) in the Cyanoacetamide **4b** and Benzonaphthyridine **6c** Structures

Angle	ω, deg	Angle	ω, deg
Cyanoacetamide **4b**		Benzonaphthyridine **6c**	
$C_{(10)}$–$O_{(3)}$–$C_{(11)}$	116.1(1)	$C_{(12)}$–$N_{(1)}$–$C_{(1)}$	120.4(2)
$C_{(9)}$–$N_{(1)}$–$C_{(16)}$	116.4(1)	$C_{(1)}$–$N_{(1)}$–$C_{(13)}$	121.3(2)
$N_{(1)}$–$C_{(1)}$–$C_{(2)}$	120.4(1)	$C_{(2)}$–$C_{(1)}$–$N_{(1)}$	119.6(2)
$C_{(2)}$–$C_{(1)}$–$C_{(6)}$	119.2(1)	$N_{(1)}$–$C_{(1)}$–$C_{(6)}$	120.9(2)
$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	121.1(2)	$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	120.4(2)
$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	121.5(2)	$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	121.7(2)
$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	123.0(1)	$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	122.8(2)
$C_{(8)}$–$C_{(7)}$–$C_{(6)}$	119.1(1)	$C_{(11)}$–$C_{(7)}$–$C_{(8)}$	118.2(2)
$C_{(6)}$–$C_{(7)}$–$C_{(13)}$	121.7(1)	$C_{(8)}$–$C_{(7)}$–$C_{(6)}$	125.8(2)
$C_{(7)}$–$C_{(8)}$–$C_{(10)}$	122.2(1)	$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	120.8(2)
$O_{(1)}$–$C_{(9)}$–$N_{(1)}$	121.2(1)	$O_{(3)}$–$C_{(9)}$–$N_{(3)}$	118.9(2)
$N_{(1)}$–$C_{(9)}$–$C_{(8)}$	117.0(1)	$N_{(3)}$–$C_{(9)}$–$C_{(8)}$	116.8(2)
$O_{(2)}$–$C_{(10)}$–$C_{(8)}$	124.0(2)	$O_{(2)}$–$C_{(10)}$–$C_{(11)}$	122.8(2)
$O_{(3)}$–$C_{(11)}$–$C_{(12)}$	112.1(2)	$C_{(7)}$–$C_{(11)}$–$C_{(12)}$	122.5(2)
$C_{(15)}$–$C_{(13)}$–$C_{(14)}$	110.4(1)	$C_{(12)}$–$C_{(11)}$–$C_{(10)}$	116.4(2)
$O_{(4)}$–$C_{(14)}$–$N_{(3)}$	125.9(2)	$O_{(1)}$–$C_{(12)}$–$C_{(11)}$	120.5(2)
$N_{(3)}$–$C_{(14)}$–$C_{(13)}$	113.2(1)	$N_{(1)}$–$C_{(13)}$–$C_{(14)}$	111.1(2)
$N_{(1)}$–$C_{(16)}$–$C_{(17)}$	113.5(2)	$N_{(2)}$–$C_{(16)}$–$C_{(8)}$	176.4(2)
$C_{(9)}$–$N_{(1)}$–$C_{(1)}$	122.3(1)	$C_{(12)}$–$N_{(1)}$–$C_{(13)}$	118.4(2)
$C_{(1)}$–$N_{(1)}$–$C_{(16)}$	121.3(1)	$C_{(10)}$–$N_{(3)}$–$C_{(9)}$	124.6(2)
$N_{(1)}$–$C_{(1)}$–$C_{(6)}$	120.3(1)	$C_{(2)}$–$C_{(1)}$–$C_{(6)}$	119.5(2)
$C_{(3)}$–$C_{(2)}$–$C_{(1)}$	120.1(2)	$C_{(3)}$–$C_{(2)}$–$C_{(1)}$	121.0(2)
$C_{(5)}$–$C_{(4)}$-$C_{(3)}$	119.4(2)	$C_{(5)}$–$C_{(4)}$–$C_{(3)}$	119.3(2)
$C_{(5)}$–$C_{(6)}$–$C_{(1)}$	118.7(1)	$C_{(5)}$–$C_{(6)}$–$C_{(1)}$	118.0(2)
$C_{(1)}$–$C_{(6)}$–$C_{(7)}$	118.3(1)	$C_{(1)}$–$C_{(6)}$–$C_{(7)}$	119.1(2)
$C_{(8)}$–$C_{(7)}$–$C_{(13)}$	119.1(1)	$C_{(11)}$–$C_{(7)}$–$C_{(6)}$	116.0(2)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	122.4(1)	$C_{(7)}$–$C_{(8)}$–$C_{(16)}$	126.0(2)
$C_{(9)}$–$C_{(8)}$–$C_{(10)}$	115.4(1)	$C_{(16)}$–$C_{(8)}$–$C_{(9)}$	113.1(2)
$O_{(1)}$–$C_{(9)}$–$C_{(8)}$	121.8(1)	$O_{(3)}$–$C_{(9)}$–$C_{(8)}$	124.3(2)
$O_{(2)}$–$C_{(10)}$–$O_{(3)}$	125.2(2)	$O_{(2)}$–$C_{(10)}$–$N_{(3)}$	119.0(2)
$O_{(3)}$–$C_{(10)}$–$C_{(8)}$	110.7(1)	$N_{(3)}$–$C_{(10)}$–$C_{(11)}$	118.3(2)
$C_{(15)}$–$C_{(13)}$–$C_{(7)}$	111.2(1)	$C_{(7)}$–$C_{(11)}$–$C_{(10)}$	121.1(2)
$C_{(7)}$–$C_{(13)}$–$C_{(14)}$	116.0(1)	$O_{(1)}$–$C_{(12)}$–$N_{(1)}$	119.1(2)
$O_{(4)}$–$C_{(14)}$–$C_{(13)}$	120.9(2)	$N_{(1)}$–$C_{(12)}$–$C_{(11)}$	120.4(2)
$N_{(2)}$–$C_{(15)}$–$C_{(13)}$	176.2(2)	$C_{(13)}$–$C_{(14)}$–$C_{(15)}$	111.0(2)

The repulsion between the substituent on the $N_{(1)}$ atom, the neighboring carbonyl group, and the hydrogen atom in the *peri* position of the benzene ring [shortened intramolecular contacts $H_{(2)}$…$C_{(13)}$ 2.49 (2.87), $H_{(2)}$…$H_{(13a)}$ 1.99 (2.34), $H_{(13a)}$…$C_{(2)}$ 2.58 (2.87), and $H_{(13b)}$…$C_{(2)}$ 2.21 (2.46 Å)] means that the propyl group is perpendicular to the dihydro ring plane (torsional angle $C_{(12)}$–$N_{(1)}$–$C_{(13)}$–$C_{(14)}$ -98.6(2)º).

In the crystal the benzonaphthyridine **6c** forms centrosymmetric dimers *via* an intermolecular hydrogen bond $N_{(3)}$–$H_{(3N)}$…$O_{(3)'}$ (-*x*, -*y*, -*z*) H…O 1.88 Å, N–H…O 177º which also leads to shortening of the $O_{(3)}$–$C_{(9)}$ bond 1.239(3) Å (mean value 1.210 Å). The crystal also shows a weak intermolecular hydrogen bond $C_{(2}$–$H_{(2)}$…$N_{(2)}$ (-*x*, 0.5+*y*, 0.5-*z*) H…N 2.46 Å, C–H…N 164º and shortened intermolecular contacts $H_{(3N)}$…$C_{(9)'}$ (-*x*, -*y*, -*z*) 2.80 (2.87), $H_{(15)}$…$C_{(9)}$ (0.5-*x*, 0.5+*y*, *z*) 2.83 (2.87 Å).

EXPERIMENTAL

^{1}H NMR spectra for the compounds synthesized were recorded on a Varian Mercury VX-200 instrument (200 MHz) using DMSO-d_6 solvent and TMS internal standard. The mass spectra of the benzonaphthyridines **6** were taken on a Varian 1200L spectrometer with total scanning in the range 35-700 *m/z*, ionization 70 eV, and with direct introduction.

Ethyl 1-R-4-(carbamoylcyanomethyl)-2-oxo-1,2-dihydroquinoline-3-carboxylate 4 (General Method). The corresponding ethyl 1-R-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**, 0.01 mol), malononitrile (0.72 g, 0.011 mol), and K_2CO_3 (2 g) in DMF (15 ml) became considerably hot several minutes after mixing. The reaction was completed by heating at 50ºC for 3-4 h. The product was cooled, diluted with cold water, and acidified to pH 4 with HCl. The precipitated cyanoacetamide **4** was filtered off, washed with water, dried, and crystallized from ethanol.

6-R-5-Hydroxy-2,4-dioxo-2,3,4,6-tetrahydrobenzo[*c*][2,7]naphthyridine-1-carbonitriles 6 (General Method). The cyanoacetamide **4** (0.01 mol) in 10% aqueous KOH solution (30 ml) was heated to reflux and then refluxed for 15-20 min. The initially strong yellow color of the solution rapidly disappeared and a colorless precipitate was formed. The reaction mixture was cooled and the precipitated benzonaphthyridine **6** was filtered off, washed with water, dried, and crystallized from DMF.

X-Ray Investigation. Crystals of the cyanoacetamide **4b** were obtained from ethanol and are triclinic. At -173ºC: a = 8.414(2), b = 10.282(2), c = 10.594(3) Å, α = 113.35(2), β = 90.77(2), γ = 108.05(2), V = 790.3(3) Å^3, M_r = 327.34, Z = 2, space group $P\bar{1}$, d_{calc} = 1.376 g/cm^3, μ(MoKα) = 0.100 mm^{-1}, F(000) = 344. Crystals of the benzonaphthyridine **6c** were obtained from DMSO and are rhombic. At -173ºC: a = 7.3067(8), b = 17.890(2), c = 20.034(2) Å, V = 2618.8(5) Å^3, M_r = 295.29, Z = 8, space group P_{bca}, d_{calc} = 1.498 g/cm^3, μ(MoKα) = 0.106 mm^{-1}, F(000) = 1232. Unit cell parameters and intensities of 13522 reflections (4622 independent, R_{int} = 0.052) for cyanoacetamide **4b** and 20752 (2324 independent, R_{int} = 0.069) for benzonaphthyridine **6c** were measured on an Xcalibur-3 diffractometer (MoKα. CCD detector, graphite monochromator, ω scanning, $2\theta_{max}$ = 60 and 50º respectively).

Both structures were solved by a direct method using the SHELXTL program [10]. The positions of the hydrogen atoms were revealed in electron difference synthesis and refined isotropically. The structures were refined in F^2 full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 = 0.185 for 4541 reflections (R_1 = 0.071for 3422 reflections with $F > 4\sigma$ (F), S = 1.067) for the cyanoacetamide **4b** and to wR_2 = 0.116 for 2239 reflections (R_1 = 0.053 for 2113 reflections with $F > 4\sigma$ (F), S = 1.113) for the benzonaphthyridine **6c**. The full crystallographic information has been placed in the Cambridge structural data bank (cyanoacetamide **4b** reference CCDC 283296 and benzonaphthyridine **6c** reference CCDC 283297).

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