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# 4-HYDROXY-2-QUINOLONES. 96*. SYNTHESIS AND PROPERTIES OF 4-METHYL-2-OXO-1,2-DIHYDROQUINOLINE-3-CARBOXYLIC ACID

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*Alkaline hydrolysis of the ethyl ester of 4-(cyanoethoxycarbonylmethyl)-2-oxo-1,2-dihydroquinoline-3-carboxylic acid is accompanied by decarboxylation with loss of two molecules of $CO_2$ and leads to 4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid.*

**Keywords:** 4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid, cyanoacetic ester, 4-chloroquinoline, amidation, hydrolysis, decarboxylation, X-ray structural analysis.

In organic chemistry the method of forming new carbon-carbon bonds based on the ability of carbanions, obtained from active methylene compounds, to react readily by substitution with alkylating agents and other reactive halogen-containing substances, has been known for a long time and is widely used for preparative purposes. Hydrolysis of the substituted malonic, cyanoacetic, or acetoacetic esters synthesized in such a way, gives the corresponding acids, distinguished by an inclination to decarboxylate on heating. The whole chain of conversions based on these reactions in fact represents a simple and effective means of substituting halogen in a molecule by $CH_2COOH$ or $CH_2COR$ [2].

We noted previously the ease of forming 4-alkyl(or aryl)amino-substituted 3-ethoxycarbonyl-2-oxo-1,2-dihydroquinolines on interacting the ethyl ester of 4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**1**) with alkylamines [3], or anilines [4]. This circumstance permits the suggestion that the 4-chloro-substituted ester **1** also possesses adequate reactivity for reaction with C-nucleophiles, such as the carbanion generated in the presence of bases from cyanoacetic ester.

As experiments carried out by us showed this reaction is indeed feasible and the ethyl ester of 4-(cyanoethoxycarbonylmethyl)-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**2**) is formed in the system $DMF/K_2CO_3$ without any difficulty. Theoretically subsequent alkaline hydrolysis must lead to 2-(3-carboxy-2-oxo-1,2-dihydroquinolin-4-yl)malonic acid (**3**) which, in its turn, on thermal decarboxylation must form 4-carboxymethyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**4**). However, according to data of chromato-mass spectrometry, the product of hydrolysis of ester **2** unexpectedly proved to be not the substituted malonic acid **3** but a pure compound with molecular mass 203 units. The $^1$H NMR spectrum shows the presence in the sample being investigated of COOH and NH groups (broadened singlets at low field), a quinoline nucleus (four signals with typical multiplicity in the aromatic region), and a C-methyl group (singlet of intensity 3H at

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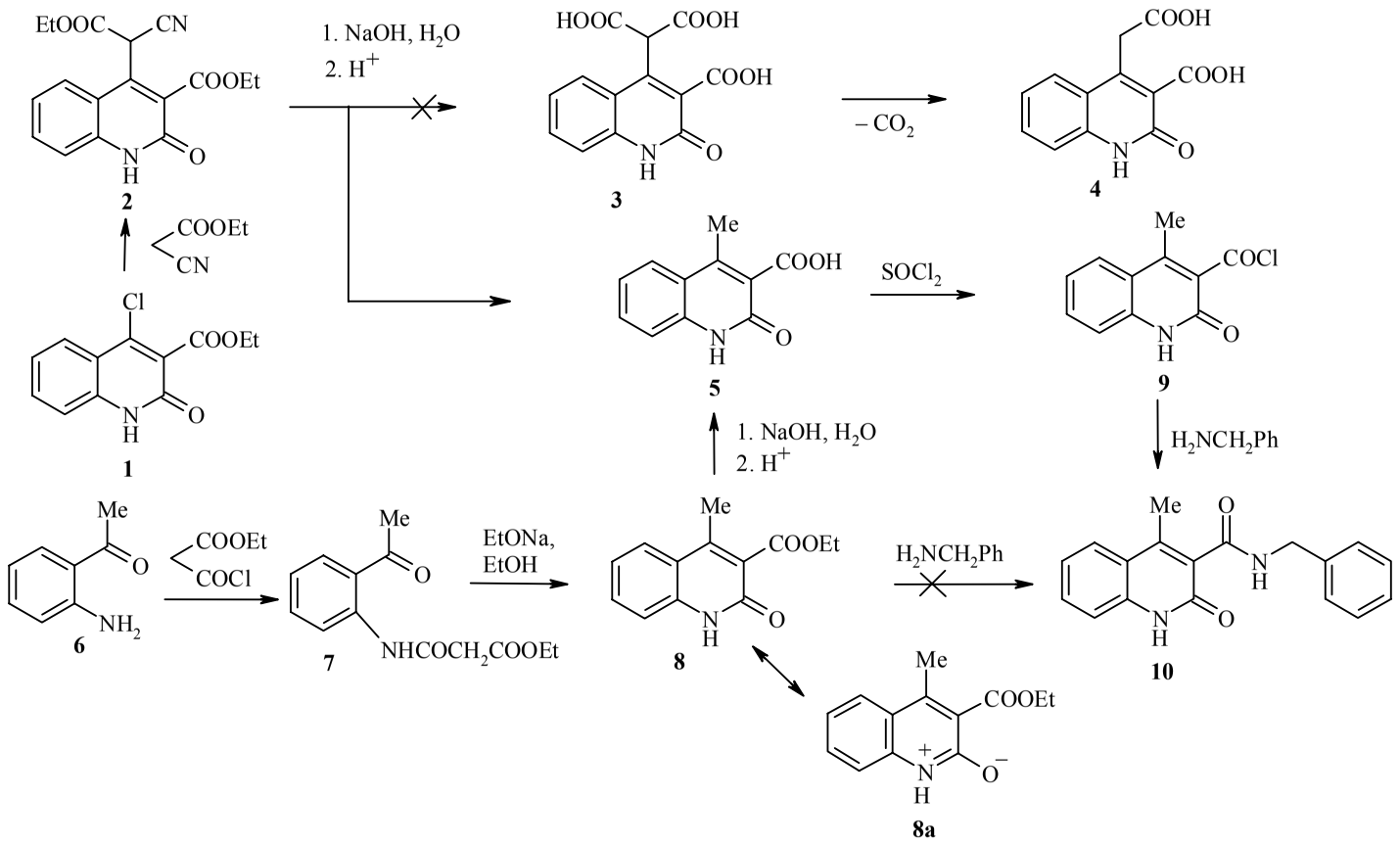
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2. H+
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1. NaOH, H2O
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COOEt
COCl
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EtONa,
EtOH
Me
COOEt
8
H2NCH2Ph
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Me
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2.55 ppm). In the initial quinolone **2** the sole source of a $CH_3$ group can only be the residue of cyanoacetic ester. Probably due to the powerful electron-withdrawing effect of the carboxyquinolone fragment, it is decarboxylated straight after hydrolysis, by a somewhat unusual route losing not one but two molecules of $CO_2$.

The product of alkaline hydrolysis of ester **2** may therefore be identified as 4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**5**). To confirm such a conclusion we synthesized acid **5** by another method, excluding any possible variants in the interpretation of its structure. With this aim *o*-aminoacetophenone (**6**) was acylated with ethoxymalonyl chloride. The obtained 2-acetylanilide **7** was converted by treatment with sodium ethylate in absolute alcohol into the ethyl ester of 4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**8**), after hydrolysis of which acid **5** was isolated, identical in its properties and spectral characteristics with the sample described above.

Unlike the esters of 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid [5], their 4-methyl-substituted analog **8** was hydrolyzed fairly readily, and at the same time was completely inert to amidation by alkylamines under the usual conditions. The reason for such a significant difference in reactivity is evidently the impossibility of ester **8** to form salts of the type of the 4-hydroxy derivatives [6] with cations of the alkali metals, stable to the action of nucleophiles in the first case and the special features of the spatial disposition of the ester grouping in the second.

In the previously studied ethyl esters of 1-R-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acids [7-9] the ethoxycarbonyl group was always coplanar with the quinoline plane as a result of the formation of intramolecular hydrogen bonds with the hydroxyl group. Replacement of the hydroxyl group by methyl leads to the fact that in the molecule of ester **8** (see Fig. 1 and Tables 1, 2) the ester substituent is folded practically perpendicularly to the quinoline plane [torsion angle $O_{(2)}$–$C_{(10)}$–$C_{(8)}$–$C_{(7)}$ 101.4(6)°], which also explains its inertness towards the action of alkylamines. The $C_{(11)}$ atom of the ester group is in the *ap* position relative to the $C_{(10)}$–$C_{(8)}$ bond and the $C_{(12)}$ atom is in a position very close to the *ap* position relative to the $C_{(10)}$–$O_{(3)}$ bond [torsion angle $C_{(11)}$–$O_{(3)}$–$C_{(10)}$–$C_{(8)}$ is 176.8(4)°, $C_{(10)}$–$O_{(3)}$–$C_{(11)}$–$C_{(12)}$ is 170.2(5)°]. The repulsion between the methyl group at the $C_{(7)}$ atom, the $C_{(10)}$ atom, and the atoms of the aromatic ring, shown by the shortened intramolecular contacts $H_{(13c)}$···$C_{(10)}$ 2.44 (sum of van der Waals radii 2.87 [10], $H_{(5a)}$···$C_{(13)}$ 2.63 (2.87) and $H_{(13a)}$···$C_{(5)}$ 2.83 Å (2.87 Å), leads to a some twisting of the $C_{(7)}$-$C_{(8)}$ double bond [torsion angle $C_{(13)}$–$C_{(7)}$–$C_{(8)}$–$C_{(10)}$ 4.2(6)°].

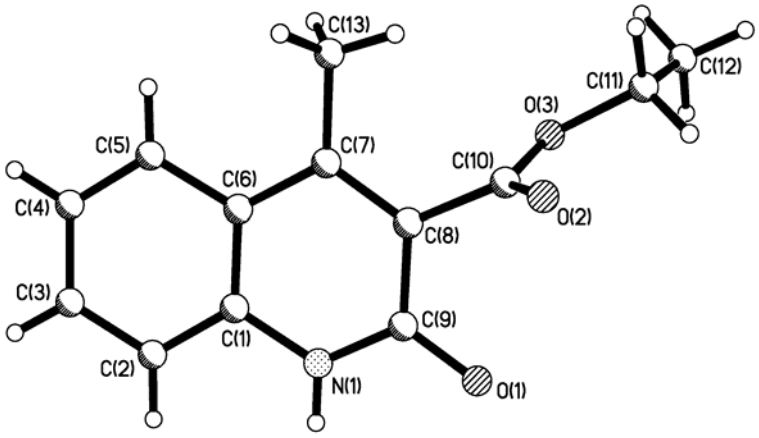


Fig. 1. Structure of the molecule of ester **8** with numbering of atoms.

TABLE 1. Bond Lengths (*l*) in the Structure of Ester **8**

| Bond | *l*, Å | Bond | *l*, Å | Bond | *l*, Å |
|---|---|---|---|---|---|
| $N_{(1)}$–$C_{(9)}$ | 1.343(5) | $C_{(6)}$–$C_{(7)}$ | 1.429(6) | $C_{(1)}$–$C_{(2)}$ | 1.386(6) |
| $O_{(1)}$–$C_{(9)}$ | 1.261(6) | $C_{(7)}$–$C_{(13)}$ | 1.477(7) | $C_{(3)}$–$C_{(4)}$ | 1.365(7) |
| $O_{(3)}$–$C_{(10)}$ | 1.328(5) | $C_{(8)}$–$C_{(10)}$ | 1.488(6) | $C_{(5)}$–$C_{(6)}$ | 1.435(7) |
| $C_{(1)}$–$C_{(6)}$ | 1.379(6) | $N_{(1)}$–$C_{(1)}$ | 1.402(6) | $C_{(7)}$–$C_{(8)}$ | 1.382(6) |
| $C_{(2)}$–$C_{(3)}$ | 1.384(7) | $O_{(2)}$–$C_{(10)}$ | 1.189(5) | $C_{(8)}$–$C_{(9)}$ | 1.421(6) |
| $C_{(4)}$–$C_{(5)}$ | 1.380(6) | $O_{(3)}$–$C_{(11)}$ | 1.449(6) | $C_{(11)}$–$C_{(12)}$ | 1.461(7) |

TABLE 2. Valence Angles (ω) in the Structure of Ester **8**

| Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|
| $C_{(9)}$–$N_{(1)}$–$C_{(1)}$ | 122.5(4) | $C_{(10)}$–$O_{(3)}$–$C_{(11)}$ | 117.0(4) |
| $C_{(6)}$–$C_{(1)}$–$C_{(2)}$ | 123.5(4) | $C_{(6)}$–$C_{(1)}$–$N_{(1)}$ | 118.7(4) |
| $C_{(2)}$–$C_{(1)}$–$N_{(1)}$ | 117.8(4) | $C_{(3)}$–$C_{(2)}$–$C_{(1)}$ | 118.4(5) |
| $C_{(4)}$–$C_{(3)}$–$C_{(2)}$ | 120.2(5) | $C_{(3)}$–$C_{(4)}$–$C_{(5)}$ | 121.8(5) |
| $C_{(4)}$–$C_{(5)}$–$C_{(6)}$ | 119.5(5) | $C_{(1)}$–$C_{(6)}$–$C_{(7)}$ | 120.8(4) |
| $C_{(1)}$–$C_{(6)}$–$C_{(5)}$ | 116.6(4) | $C_{(7)}$–$C_{(6)}$–$C_{(5)}$ | 122.5(5) |
| $C_{(8)}$–$C_{(7)}$–$C_{(6)}$ | 117.8(5) | $C_{(8)}$–$C_{(7)}$–$C_{(13)}$ | 121.8(4) |
| $C_{(6)}$–$C_{(7)}$–$C_{(13)}$ | 120.3(4) | $C_{(7)}$–$C_{(8)}$–$C_{(9)}$ | 121.3(4) |
| $C_{(7)}$–$C_{(8)}$–$C_{(10)}$ | 121.3(4) | $C_{(9)}$–$C_{(8)}$–$C_{(10)}$ | 117.2(4) |
| $O_{(1)}$–$C_{(9)}$–$N_{(1)}$ | 119.5(4) | $O_{(1)}$–$C_{(9)}$–$C_{(8)}$ | 121.8(4) |
| $N_{(1)}$–$C_{(9)}$–$C_{(8)}$ | 118.7(4) | $O_{(2)}$–$C_{(10)}$–$O_{(3)}$ | 123.4(5) |
| $O_{(2)}$–$C_{(10)}$–$C_{(8)}$ | 123.9(4) | $O_{(3)}$–$C_{(10)}$–$C_{(8)}$ | 112.6(4) |
| $O_{(3)}$–$C_{(11)}$–$C_{(12)}$ | 109.7(5) | | |

The bicyclic fragment of ester **8** is planar with a precision of 0.02 Å. The noticeable extension of the $C_{(7)}$–$C_{(8)}$ bond to 1.382(6) and the $O_{(1)}$–$C_{(9)}$ bond to 1.261(6) Å compared with their mean values of 1.326 and 1.210 Å respectively [11], and the shortening of the $C_{(8)}$–$C_{(9)}$ bond to 1.421(6) (mean value 1.455) and the $N_{(1)}$–$C_{(9)}$ bond to 1.343(5) Å (1.385 Å) permits the suggestion that the structure of the ethyl ester of 4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid is described as a hybrid of two resonance structures **8** and **8a** with a predominant contribution of structure **8**. Dimers form in the crystal of the molecule of this compound as a result of the intermolecular hydrogen bond $N_{(1)}$–$H_{(1a)}$···$O_{(1)}$, (1 - *x*, -*y*, -*z*) H···O 1.93 Å, N–H···O 168°.

As is known [12], treatment of 1-H-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylic acid with thionyl chloride gives a mixture of the acid chlorides of 4-chloro-2-oxo- and 2,4-dichloroquinoline-3-carboxylic acids. In the case of acid **5** such an effect was not observed, and as shown in the example of benzylamine, the appropriate amides **10** may be obtained in high yield through acid chloride **9**.

## EXPERIMENTAL

The $^1$H NMR spectra of the synthesized compounds were recorded on a Varian Mercury VX-200 (200 MHz) instrument, solvent was DMSO-$d_6$, internal standard was TMS. Chromato-mass spectra were recorded on a Finnigan MAT Incos 50 quadrupole spectrometer in total scanning mode in the range 33-700 *m/z*, ionization by electron capture at 70 eV with direct insertion of samples, rate of heating was ~5°C/sec. The ethyl ester of acid **1** was obtained by the known procedure of [13]. Commercial *o*-aminoacetophenone from Aldrich was used in the synthesis of the ethyl ester of acid **8**.

**Ethyl Ester of 4-(Cyanoethoxycarbonylmethyl)-2-oxo-1,2-dihydroquinoline-3-carboxylic Acid (2).** A mixture of the ethyl ester of 4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (**1**) (2.51 g, 0.01 mmol), cyanoacetic ester (1.17 ml, 0.011 mol), and $K_2CO_3$ (2 g) in DMF (15 ml) was stirred for 10 h at 90°C. After cooling, the reaction mixture was diluted with water, and acidified with HCl to pH 5. The precipitated solid ester **2** was filtered off, washed with water, and dried. Yield 2.92 g (89%); mp 183-185°C (ethanol). Mass spectrum, *m/z* ($I_{rel}$, %): 328 (26) $[M]^+$, 283 (15) $[M\text{-}OEt]^+$, 255 (37) $[M\text{-}OEt\text{-}CO]^+$, 254 (100) $[M\text{-}OEt\text{-}HCO]^+$, 227 (18) $[M\text{-}OEt\text{-}HCO\text{-}HCN]^+$, 210 (85) $[M\text{-}OEt\text{-}CO\text{-}OEt]^+$, 184 (40), 127 (44). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 12.46 (1H, s, NH); 7.79 (1H, d, *J* = 8.2, H-5); 7.65 (1H, td, *J* = 7.6 and *J* = 1.0, H-7); 7.41 (1H, d, *J* = 8.1, H-8); 7.32 (1H, td, *J* = 7.9 and *J* = 1.0, H-6); 6.20 (1H, s, CH–CN); 4.31 (2H, q, *J* = 7.2, $OCH_2$); 4.19 (2H, q, *J* = 7.2, $CHCOOC\underline{H}_2$); 1.27 (3H, t, *J* = 7.2, $CH_3$); 1.13 (3H, t, *J* = 7.2, $CHCOOCH_2C\underline{H}_3$). Found, %: C 62.30; H 4.97; N 8.40. $C_{17}H_{16}N_2O_5$. Calculated, %: C 62.19; H 4.91; N 8.53.

**4-Methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic Acid (5).** A mixture of compound **2** (3.28 g, 0.01 mol) and aqueous 20% NaOH solution (30 ml) was boiled until the end of evolution of ammonia (~10 h). The mixture was cooled, and acidified with HCl to pH 3. The precipitated acid **5** was filtered off, washed with water, and dried. Yield 1.84 g (91%); mp 274-276°C (ethanol). Mass spectrum, *m/z* ($I_{rel}$, %): 203 (76) $[M]^+$, 185 (100) $[M\text{-}H_2O]^+$, 159 (98) $[M\text{-}CO_2]^+$, 141 (36) $[M\text{-}H_2O\text{-}CO_2]^+$, 130 (35), 77 (39), 44 (58). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 13.84 (1H, s, COOH); 12.20 (1H, s, NH); 7.87 (1H, d, *J* = 8.2, H-5); 7.59 (1H, t, *J* = 7.4, H-7); 7.36 (1H, d, *J* = 7.8, H-8); 7.27 (1H, t, *J* = 7.5, H-6); 2.55 (3H, s, $CH_3$). Found, %: C 65.18; H 4.57; N 6.77. $C_{11}H_9NO_3$. Calculated, %: C 65.02; H 4.46; N 6.89.

A mixing test with a sample of acid **5**, obtained by alkaline hydrolysis of the ethyl ester of acid **8** by an analogous method, gave no depression of melting point. The $^1$H NMR and chromato-mass spectra of these compounds were identical.

**Ethyl Ester of 4-Methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic Acid (8).** Triethylamine (15.4 ml, 0.11 mol) was added to a solution of 2-aminoacetophenone **6** (13.5 g, 0.1 mol) in $CH_2Cl_2$ (100 ml), then ethoxymalonyl chloride (16.56 g, 0.11 mol) was added dropwise with stirring and cooling, and the mixture maintained at room temperature for 4-5 h. The reaction mixture was then diluted with water, the organic layer was separated, and dried over anhydrous $CaCl_2$. The solvent was distilled (at reduced pressure towards the end). A solution of sodium ethylate [from metallic sodium (3.45 g, 0.15 mol) in absolute ethyl alcohol (150 ml)], was added to the residue (2-acetylanilide **7**), the mixture was boiled for 1 h on a water bath, after which the heating was stopped, and the mixture left for 7-8 h at room temperature. The reaction mixture was diluted with water, and acidified with dilute (1:1) HCl to pH 4.5-5. The precipitate of ester **8** was filtered off, washed with cold water, and dried. Yield 22.0 g (95%); mp 251-253°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 11.85 (1H, s, NH); 7.79 (1H, dd, *J* = 8.2 and *J* = 0.8, H-5); 7.55 (1H, td, *J* = 7.6 and *J* = 1.0, H-7); 7.33 (1H, dd, *J* = 8.0 and *J* = 0.6, H-8); 7.23 (1H, td, *J* = 7.5 and *J* = 0.8, H-6); 4.30 (2H, q, *J* = 7.1, $OCH_2$); 2.38 (3H, s, $CH_3$); 1.29 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$). Found, %: C 67.65; H 5.77; N 6.14. $C_{13}H_{13}NO_3$. Calculated, %: C 67.52; H 5.67; N 6.06.

**Benzylamide of 4-Methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic Acid (10).** Thionyl chloride (1.44 ml, 0.02 mol) was added to a solution of acid **5** (2.03 g, 0.01 mol) in dry $CCl_4$ (20 ml) and the mixture boiled with prevention of air moisture until the end of HCl and $SO_2$ evolution (~2 h). The solvent and the excess of $SOCl_2$ were then distilled off (at the end under reduced pressure). The residue (acid chloride **9**) was dissolved in dry acetone (20 ml) and the obtained solution was added dropwise with stirring and cooling to a mixture of benzylamine (1.09 ml, 0.01 mol) and triethylamine (1.4 ml, 0.01 mol) in dry acetone (30 ml). After 3-4 h the reaction mixture was diluted with water and acidified with dilute (1:1) HCl to pH 4. The solid amide **10** was filtered off, washed with cold water, and dried. Yield 2.63 g (90%); mp 239-241°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 11.82 (1H, s, NH); 8.81 (1H, t, $N\underline{H}CH_2$); 7.77 (1H, d, *J* = 8.1, H-5); 7.52 (1H, t, *J* = 7.6, H-7); 7.16-7.44 (7H, m, H-6, 8+$C_6H_5$); 4.44 (2H, d, *J* = 6.2, $NCH_2$); 2.34 (3H, s, $CH_3$). Found, %: C 73.84; H 5.50; N 9.44. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.96; H 5.52; N 9.58.

**X-Ray Structural Investigation.** Crystals of ester **8** were monoclinic, at -109°C $a$ = 11.034(4), $b$ = 15.073(4), $c$ = 6.646(3) Å; β = 95.55(3)°; $V$ = 1100.2(7) Å$^3$; $M_r$ = 231.24; $Z$ = 4; space group $P2_1/c$; $d_{calc}$ = 1.396 g/cm$^3$; μ(MoKα) = 0.100 mm$^{-1}$, $F$(000) = 488. The parameters of the unit cell and the intensities of 2001 reflections (1915 independent, $R_{int}$ = 0.023) were measured on a Siemens P3/PC automatic four-circle diffractometer (MoKα, graphite monochromator, 2θ/θ scanning, $2\theta_{max}$ = 50°).

The structure was solved by the direct method with the SHELXTL set of programs [14]. The positions of the hydrogen atoms were calculated geometrically and refined according to the rider model with $U_{iso} = nU_{eq}$ of the nonhydrogen atom linked with the given hydrogen ($n$ = 1.5 for a methyl group and $n$ = 1.2 for the remaining hydrogen atoms). The structure was refined on $F^2$ with a full-matrix least squares method in an anisotropic approximation for the non-hydrogen atoms to $wR_2$ = 0.168 for 1744 reflections ($R_1$ = 0.066 for 751 reflections with $F > 4\sigma(F)$, $S$ = 0.985). All of the crystallographic information has been deposited in the Cambridge structural data bank (deposition No. CCDC 257525). Interatomic distances and valence angles are given in Tables 1 and 2.

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