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4-HYDROXY-2-QUINOLONES 151*. REACTION OF 4-CHLORO-3-ETHOXYCARBONYL-2-OXO-1,2-DIHYDROQUINOLINES WITH *p*-TOLUENESULFONYLHYDRAZIDE

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The reaction of ethyl 4-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate with p-toluenesulfonylhydrazide at room temperature in the system DMSO/K_2CO_3 gives 5-methyl-2-(toluene-4-sulfonyl)-1,2-dihydro-5H-pyrazolo[4,3-c]quinoline-3,4-dione, alkylation of which using ethyl iodide gives the 1N-substituted derivative.

Keywords: 1,5-dihydropyrazolo[4,3-*c*]quinolin-4-ones, 4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylates, *p*-toluenesulfonylhydrazide, alkylation, X-ray structural analysis.

The reaction of ethyl 1-R-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylates with *p*-toluenesulfonylhydrazide is extremely sensitive to the conditions used which determine its occurrence by one route or another. Hence carrying out the synthesis in 96% ethanol gave good yields of 5-substituted 3-hydroxy-1,5-dihydropyrazolo[4,3-*c*]quinolin-4-ones [2] whereas the use of anhydrous solvents unexpectedly gave the 4-tosyl derivatives of the corresponding 3-ethoxycarbonyl-2-oxo-1,2-dihydroquinolines [3]. In this case it was proposed to exchange just the chlorine atom in the starting 4-chloroquinolones for hydrogen by transformation in the first stage to β-N-hetaryl-substituted tosylhydrazides and then by basic hydrolysis in the final stage to the target 2-oxo-1,2-di-hydroquinoline-3-carboxylic acids. In both cases reported above the reactions were carried out in refluxing solvents which perhaps also served as the reason for more profound structural transformations than anticipated and so it was quite natural to try out the synthesis in comparatively milder conditions, in particular at room temperature. The studied reaction is not characterized by a high velocity, even in refluxing solvents [2, 3]. Hence at room temperature it could only successfully be performed after increasing the nucleophilic properties of the nitrogen atoms of the p-toluenesulfonylhydrazide. This can be readily achieved by the use of the base in aprotoic, bipolar solvents and principally in DMSO [4].

* For Communication 150 see [1].

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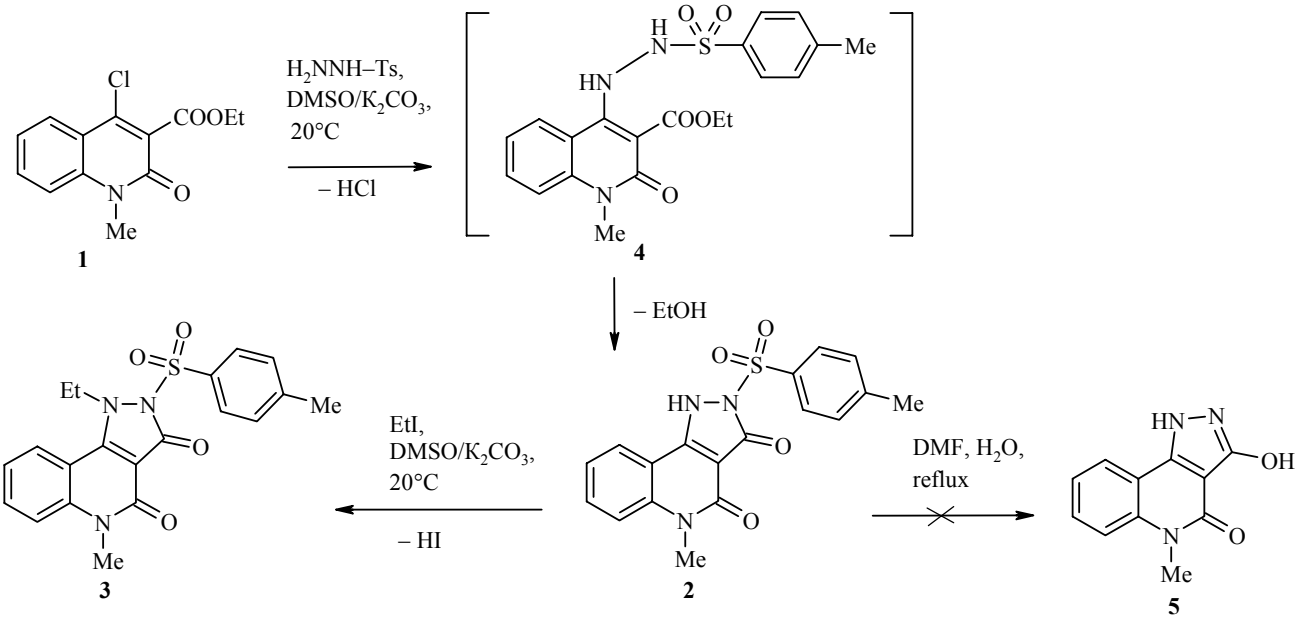
However, as shown in practice, ethyl 4-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**) and *p*-toluenesulfonylhydrazide react only slowly at room temperature, even in the system DMSO/K_2CO_3. None the less, the product of this reaction was separated and, according to ^{1}H NMR spectroscopic data, it clearly contained a quinolone ring and a *p*-toluenesulfonyl residue in its structure. However, the signals corresponding to the protons of a ethoxycarbonyl group or hydrazide residue were absent from the spectrum. The ^{13}C NMR spectrum showed 16 separate signals and, allowing the magnetic equivalence of two pairs of the carbon atoms



in the *p*-disubstituted aromatic ring, infers 18 carbon atoms in the composition of the synthetic compound. This information is clearly insufficient for an unambiguous proof of the structure of the structure studied hence we attempted its further investigation using the method of heteronuclear ^{13}C–^{1}H spectroscopy. For assignment of the protonated carbon atoms the HMQC spectra revealed the ^{13}C–^{1}H interactions through one chemical bond. The HMBC method uses the signals of the quaternary carbon atoms in the interpretation and can reveal these ^{13}C–^{1}H spin-spin interactions through 2-3 bonds. The most important HMBC correlations and signal assignments derived on their basis in the carbon spectrum for the reaction product of the chloro-substituted ester **1** and *p*-toluenesulfonylhydrazide are shown in the Scheme. The full list of all correlations found are given in Table 1.

For the two carbon signals at 90.9 and 165.3 ppm correlations with proton signals could not be found but, by analogy with preceding studies [5-7], we assign the first of these to the $C_{(3)}$ atom of the quinolone ring

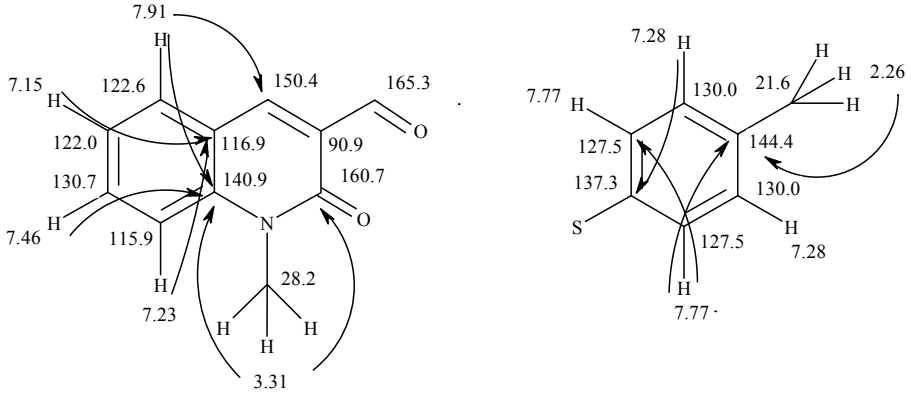


TABLE 1 ^{1}H–^{13}C Heteronuclear Correlations Found for the 1H-Pyrazolo-quinoline **2**

δ, ppm	HMQC	HMBC
7.91	122.6	150.4, 140.9, 130.7
7.77	127.5	144.4, 127.5
7.46	130.7	140.9, 122.6
7.28	130.0	137.3, 130.0, 127.5 (weak), 21.6
7.23	115.9	122.0, 116.9
7.15	122.0	116.9
3.31	28.2	160.7, 140.9, 115.9 (weak)
2.26	21.6	144.4, 137.3, 130.0

and the second to the carbonyl carbon atom contained in the ester group prior to the reaction. Hence correlation heteronuclear ^{13}C–^{1}H NMR spectroscopy confirms the presence of quinolone and *p*-toluenesulfonyl fragments in the compound studied. None the less a secure overall assignment of the structure could not be made by this method since the linking of the molecular fragments indicated could not be tracked *via* the heteronuclear correlations. This can be attributed to the presence of a separating bridge which has several noncarbon atoms and its identification evidently needs other analytical methods.

Much could be clarified from the mass spectrum but ionization by electron impact unfortunately could not be accomplished, the material proving to be unstable. With the use of milder chemical positive ionization at atmospheric pressure a peak with *m/z* 370 was indeed recorded. If one assumes that this peak is due to the protonated molecular ion and taking account of the NMR spectroscopic data then the synthesized compound is 5-methyl-2-(toluene-4-sulfonyl)-1,2-dihydro-5H-pyrazolo[4,3-*c*]quinoline-3,4-dione (**2**). In truth one question remains unanswered for this structure, i.e. the absence of the signal for the NH group proton in the ^{1}H NMR spectrum and this could not be identified despite numerous variations of the solution concentrations and their temperature.

Bearing in mind this complex situation we attempted to establish the structure of the compound studied by its chemical modification by carrying out an alkylation with ethyl iodide in the system DMSO/K_2CO_3 at room temperature. This operation proved very successful since a single crystal of the ethyl derivative could be grown which was suitable for X-ray analysis. As a result we have unambiguously shown that we are dealing with 1-ethyl-5-methyl-2-(toluene-4-sulfonyl)-1,2-dihydro-5H-pyrazolo[4,3-*c*]quinoline-3,4-dione (**3**). In its

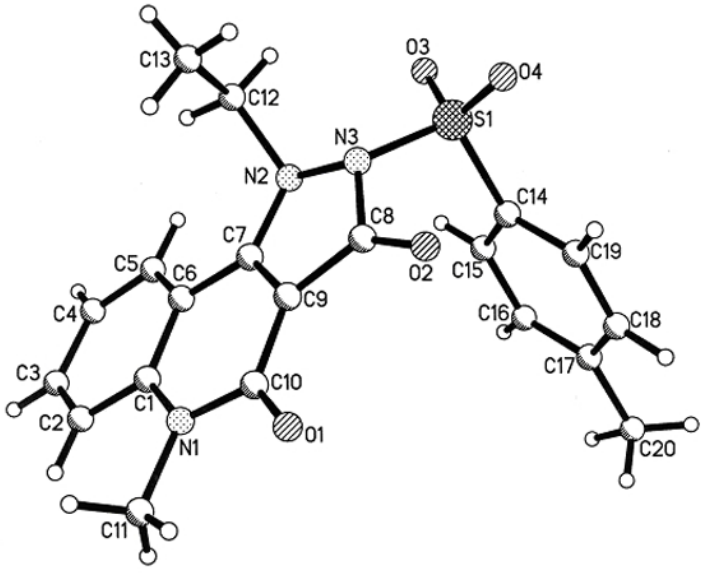


Fig. 1. Structure of the 1-ethylpyrazoloquinoline **3** with atomic numbering.

TABLE 2. Bond Lengths (*l*) in the 1-Ethylpyrazoloquinoline **3** Structure

Bond	*l*, Å	Bond	*l*, Å
$S_{(1)}–O_{(3)}$	1.417(1)	$S_{(1)}–O_{(4)}$	1.418(1)
$S_{(1)}–N_{(3)}$	1.699(2)	$S_{(1)}–C_{(14)}$	1.754(2)
$O_{(1)}–C_{(10)}$	1.222(2)	$O_{(2)}–C_{(8)}$	1.210(2)
$N_{(1)}–C_{(10)}$	1.388(2)	$N_{(1)}–C_{(1)}$	1.398(2)
$N_{(1)}–C_{(11)}$	1.471(3)	$N_{(2)}–C_{(7)}$	1.389(2)
$N_{(2)}–N_{(3)}$	1.436(2)	$N_{(2)}–C_{(12)}$	1.511(2)
$N_{(3)}–C_{(8)}$	1.445(2)	$C_{(1)}–C_{(2)}$	1.402(3)
$C_{(1)}–C_{(6)}$	1.414(3)	$C_{(2)}–C_{(3)}$	1.365(3)
$C_{(3)}–C_{(4)}$	1.384(3)	$C_{(4)}–C_{(5)}$	1.366(3)
$C_{(5)}–C_{(6)}$	1.397(3)	$C_{(6)}–C_{(7)}$	1.433(2)
$C_{(7)}–C_{(9)}$	1.357(2)	$C_{(8)}–C_{(9)}$	1.435(2)
$C_{(9)}–C_{(10)}$	1.449(2)	$C_{(12)}–C_{(13)}$	1.507(3)
$C_{(14)}–C_{(15)}$	1.380(3)	$C_{(14)}–C_{(19)}$	1.380(3)
$C_{(15)}–C_{(16)}$	1.400(4)	$C_{(16)}–C_{(17)}$	1.375(4)
$C_{(17)}–C_{(18)}$	1.361(4)	$C_{(17)}–C_{(20)}$	1.527(4)
$C_{(18)}–C_{(19)}$	1.374(3)		

structure the tricyclic fragment is not completely planar (see Figure 1 and Tables 2 and 3). The angle between the pyrazolone and benzene ring planes is 6.7º. Such a deformation of the tricyclic fragment is evidently due to the very strong repulsion between the alkyl substituents and the aromatic ring atoms (shortened intramolecular contacts $H_{(2)}\cdots C_{(11)}$ 2.46 (sum of van der Waal radii [8] 2.87), $H_{(2)}\cdots H_{(11c)}$ 2.23 (2.34), $H_{(2)}\cdots H_{(11b)}$ 2.24 (2.34), $H_{(11b)}\cdots C_{(2)}$ 2.75 (2.87), $H_{(11c)}\cdots C_{(2)}$ 2.73 (2.87), $H_{(5)}\cdots C_{(12)}$ 2.76 (2.87), $H_{(5)}\cdots H_{(12b)}$ 1.99 (2.34), $H_{(12b)}\cdots C_{(5)}$ 2.58 (2.87), and $H_{(12b)}\cdots C_{(6)}$ 2.83 Å (2.87 Å). The nitrogen atoms in the pyrazolone ring have a pyramidal configuration, the sum of valence angles centered at atoms $N_{(2)}$ and $N_{(3)}$ being 333.1 and 343.5º respectively. Analysis of literature data has shown that a pyramidal configuration of the nitrogen atoms is quite typical of pyrazolones [9-11].

The toluenesulfonyl substituent has a pseudoequatorial orientation (torsional angle $C_{(7)}–N_{(2)}–N_{(3)}–S_{(1)}$ 140.8(1)º) and it is placed such that the $S_{(1)}–O_{(3)}$ bond occurs in a conformation intermediate between *sp* and +*sc* relative to the $N_{(2}–N_{(3)}$ bond and the $S_{(1)}–O_{(4)}$ bond in a conformation close to *ap* relative to the same bond (torsional angles $O_{(3)}–S_{(1)}–N_{(3)}–N_{(2)}$ 32.0(1) and $O_{(4)}–S_{(1)}–N_{(3)}–N_{(2)}$ 160.4(1)º). The tolyl group is situated virtually perpendicularly to the $N_{(2)}–N_{(3)}$ bond (torsional angle $C_{(14)}–S_{(1)}–N_{(3)}–N_{(2)}$ -84.3(1)º) and is strongly twisted relative to the $N_{(3)}–S_{(1)}$ bond (torsional angle $N_{(3)}–S_{(1)}–C_{(14)}–C_{(15)}$ 81.9(2)º). The ethyl group occurs in a -*ac* conformation relative to the $C_{(7)}–C_{(9)}$ bond (torsional angle $C_{(12)}–N_{(2)}–C_{(7)}–C_{(9)}$ -125.0(2)º) and is twisted relative to the $C_{(7)}–N_{(2)}$ bond (torsional angle $C_{(7)}–N_{(2)}–C_{(12)}–C_{(13)}$ 66.2(2)º). This orientation of the ethyl group is likely stabilized additionally by a weak attracting interaction $H_{(12a)}\cdots O_{(3)}$ 2.44 Å (2.46 Å). The 1-ethyl-pyrazoloquinoline **3** also shows an attractive interaction $H_{(11a)}\cdots O_{(1)}$ 2.23 (2.46) and shortened intramolecular contact $H_{(16)}\cdots H_{(20c)}$ 2.30 Å (2.34 Å).

Hence from the total investigation made by us it can be confidently stated that the product of the reaction of ethyl 4-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**) with *p*-toluenesulfonyl-hydrazide in DMSO solution in the presence of K_2CO_3 is the 1H-pyrazoloquinoline **2**. The first stage of its formation can undoubtedly be considered as the β-N-quinolyl-substituted tosylhydrazide **4**. However stopping the reaction at this intermediate stage did not prove possible since in the system DMSO/K_2CO_3 the α-nitrogen atom in this compound (more strictly its N-anion) becomes a highly nucleophilic center which readily attacks the carbonyl carbon atom of the ester group resulting in an irreversible closing of a pyrazolone ring, even at room temperature. As regards the absence of an NH group signal in the ^{1}H NMR spectrum mentioned above the most likely explanation is evidently the existence of the 1H-pyrazoloquinoline **2** in the form of several tautomers with a low rate of mutual exchange.

TABLE 3. Valence Angles (ω) in the 1-Ethylpyrazoloquinoline **3** Structure

Angle	ω, deg	Angle	ω, deg
$O_{(3)}$–$S_{(1)}$–$O_{(4)}$	120.5(1)	$O_{(3)}$–$S_{(1)}$–$N_{(3)}$	105.9(1)
$O_{(4)}$–$S_{(1)}$–$N_{(3)}$	104.8(1)	$O_{(3)}$–$S_{(1)}$–$C_{(14)}$	110.1(1)
$O_{(4)}$–$S_{(1)}$–$C_{(14)}$	109.6(1)	$N_{(3)}$–$S_{(1)}$–$C_{(14)}$	104.7(1)
$C_{(10)}$–$N_{(1)}$–$C_{(1)}$	123.4(2)	$C_{(10)}$–$N_{(1)}$–$C_{(11)}$	117.2(2)
$C_{(1)}$–$N_{(1)}$–$C_{(11)}$	119.4(2)	$C_{(7)}$–$N_{(2)}$–$N_{(3)}$	104.5(1)
$C_{(7)}$–$N_{(2)}$–$C_{(12)}$	118.2(1)	$N_{(3)}$–$N_{(2)}$–$C_{(12)}$	110.3(1)
$N_{(2)}$–$N_{(3)}$–$C_{(8)}$	109.6(1)	$N_{(2)}$–$N_{(3)}$–$S_{(1)}$	115.0(1)
$C_{(8)}$–$N_{(3)}$–$S_{(1)}$	118.9(1)	$N_{(1)}$–$C_{(1)}$–$C_{(2)}$	120.2(2)
$N_{(1)}$–$C_{(1)}$–$C_{(6)}$	121.5(2)	$C_{(2)}$–$C_{(1)}$–$C_{(6)}$	118.3(2)
$C_{(3)}$–$C_{(2)}$–$C_{(1)}$	120.4(2)	$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	121.3(2)
$C_{(5)}$–$C_{(4)}$–$C_{(3)}$	119.6(2)	$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	120.8(2)
$C_{(5)}$–$C_{(6)}$–$C_{(1)}$	119.5(2)	$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	124.6(2)
$C_{(1)}$–$C_{(6)}$–$C_{(7)}$	115.8(2)	$C_{(9)}$–$C_{(7)}$–$N_{(2)}$	112.5(2)
$C_{(9)}$–$C_{(7)}$–$C_{(6)}$	121.4(2)	$N_{(2)}$–$C_{(7)}$–$C_{(6)}$	126.1(2)
$O_{(2)}$–$C_{(8)}$–$C_{(9)}$	133.4(2)	$O_{(2)}$–$C_{(8)}$–$N_{(3)}$	122.2(2)
$C_{(9)}$–$C_{(8)}$–$N_{(3)}$	104.3(1)	$C_{(7)}$–$C_{(9)}$–$C_{(8)}$	108.9(2)
$C_{(7)}$–$C_{(9)}$–$C_{(10)}$	123.4(2)	$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	127.7(2)
$O_{(1)}$–$C_{(10)}$–$N_{(1)}$	121.3(2)	$O_{(1)}$–$C_{(10)}$–$C_{(9)}$	124.3(2)
$N_{(1)}$–$C_{(10)}$–$C_{(9)}$	114.3(2)	$C_{(13)}$–$C_{(12)}$–$N_{(2)}$	113.6(2)
$C_{(15)}$–$C_{(14)}$–$C_{(19)}$	119.6(2)	$C_{(15)}$–$C_{(14)}$–$S_{(1)}$	120.2(2)
$C_{(19)}$–$C_{(14)}$–$S_{(1)}$	120.2(2)	$C_{(14)}$–$C_{(15)}$–$C_{(16)}$	119.0(3)
$C_{(17)}$–$C_{(16)}$–$C_{(15)}$	121.1(3)	$C_{(18)}$–$C_{(17)}$–$C_{(16)}$	118.7(3)
$C_{(18)}$–$C_{(17)}$–$C_{(20)}$	122.0(4)	$C_{(16)}$–$C_{(17)}$–$C_{(20)}$	119.3(4)
$C_{(17)}$–$C_{(18)}$–$C_{(19)}$	121.6(3)	$C_{(18)}$–$C_{(19)}$–$C_{(14)}$	120.1(3)

An attempt to remove the tosyl group from the 1H-pyrazoloquinoline **2** molecule by prolonged refluxing in aqueous DMF to form the previously reported 3-hydroxy-5-methyl-1,5-dihydropyrazolo[4,3-*c*]quinolin-4-one (**5**) [2] proved unsuccessful. This proves additional evidence for the proposal presented by us that, in the reaction of 4-chloro-3-ethoxycarbonyl-1,2-dihydroquinolines with *p*-toluenesulfonylhydrazide in refluxing aqueous ethanol, the removal of tosyl protection occurs exclusively prior to closure of the pyrazole ring [2]. In addition, whether the β-N-quinolyl substituted tosylhydrazide **4** formed under these conditions (in contrast to those presented in our present work) or indeed the *p*-toluenesulfonylhydrazide slowly hydrolyzing to hydrazine then takes part in the reaction with the chloroquinoline remains an open question.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra of the synthesized compounds and HMQC ad HMBC heteronuclear correlation experiments were recorded on a Varian Mercury-400 spectrometer (400 and 100 MHz respectively). All of the 2D experiments were carried out with gradient selection of useful signals. The mixing times in the pulse sequences were $^{1}J_{CH}$ = 140 and $^{2\text{-}3}J_{CH}$ = 8 Hz. The numbers of increments were 128 in the HMQC and 400 in the HMBC spectra. In all cases DMSO-d_6 was used as solvent and TMS as internal standard. The chromato-mass spectrum of the 1H-pyrazoloquinoline **2** was recorded on an Agilent 1100 LC/MSD spectrometer using APCI ionization (chemical positive ionization at atmospheric pressure). The chromatographic column parameters were: length 50 mm, diameter 4.6 mm, stationary phase ZORBAX Eclipse XDB-C18, solvent aqueous acetonitrile with 0.1% trifluoroacetic acid, gradient elution, and rate of solvent flow 2.4 ml/min. Commercial *p*-toluenesulfonylhydrazide was used from the Aldrich company in this work.

5-Methyl-2-(toluene-4-sulfonyl)-1,2-dihydro-5H-pyrazolo[4,3-*c*]quinoline-3,4-dione (2). A mixture of the 4-chloro-substituted ester **1** (2.65 g, 0.01 mol), *p*-toluenesulfonylhydrazide (1.86 g, 0.01 mol) and finely divided K_2CO_3 (3 g) in DMSO (20 ml) was stirred for 20 days at room temperature. The reaction mixture was thus changed to a gelatinous mass. Cold water (100 ml) was added and the product was then acidified using dilute (1:1) HCl to pH 5. The precipitated solid was filtered off, washed with cold water, and dried. Recrystallization from DMF gave the 1H-pyrazoloquinoline **2** (2.62 g, 71%) as colorless crystals with mp 357ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.91 (1H, dd, *J* = 7.7 and *J* = 1.6, H-9); 7.77 (2H, d, *J* = 8.5, H-2',6'); 7.46 (1H, td, *J* = 7.8 and *J* = 1.6, H-7); 7.28 (2H, d, *J* = 8.5, H-3',5'); 7.23 (1H, d, *J* = 8.8, H-6); 7.15 (1H, td, *J* = 7.4 and *J* = 1.2, H-8); 3.31 (3H, s, NCH_3); 2.26 (3H, s, Ar–CH_3). ^{13}C NMR spectrum, δ, ppm: 165.3 ($C_{(3)}$), 160.7 ($C_{(4)}$), 150.4 ($C_{(9b)}$), 144.4 ($C_{(4')}$), 140.9 ($C_{(5a)}$), 137.3 ($C_{(1')}$), 130.7 ($C_{(7)}$), 130.0 ($C_{(3',5')}$), 127.5 ($C_{(2',6')}$), 122.6 ($C_{(9)}$), 122.0 ($C_{(8)}$), 116.9 ($C_{(9a)}$), 115.9 ($C_{(6)}$), 90.9 ($C_{(3a)}$), 28.2 (NCH_3), 21.6 (Ar–CH_3). Mass spectrum, *m/z* (I_{rel}, %): 370 $[M+H]^+$ (100), 137 (15). Found, %: C 58.61; H 4.18; N 11.30. $C_{18}H_{15}N_3O_4S$. Calculated, %: C 58.53; H 4.09; N 11.38.

1-Ethyl-5-methyl-2-(toluene-4-sulfonyl)-1,2-dihydro-5H-pyrazolo[4,3-*c*]quinoline-3,4-dione (3). Finely divided K_2CO_3 (3 g) was added to a solution of the 1H-pyrazoloquinoline **2** (3.69 g, 0.01 mol) in DMSO (30 ml) followed by ethyl iodide (1.04 ml, 0.013 mmol) and the product was stirred at room temperature for 20 h. The reaction mixture was diluted with cold water and acidified with dilute (1:1) HCl to pH 5. The precipitated 1-ethylpyrazoloquinoline **3** was filtered off, washed with cold water, and dried to give product (3.69 g, 93%) with mp 246-248ºC (DMF). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 8.0, H-9); 7.84 (1H, t, *J* = 7.6, H-7); 7.77 (2H, d, *J* = 8.4, H-2',6'); 7.60 (1H, d, *J* = 8.8, H-6); 7.42 (1H, t, *J* = 7.6, H-8); 7.36 (2H, d, *J* = 8.4, H-3',5'); 4.44 (2H, q, *J* = 7.2, $NC\underline{H}_2CH_3$); 3.47 (3H, s, NCH_3); 2.29 (3H, s, Ar–CH_3); 0.88 (3H, t, *J* = 7.2, $NCH_2C\underline{H}_3$). Found, %: C 60.52; H 4.87; N 10.65. $C_{20}H_{19}N_3O_4S$. Calculated, %: C 60.44; H 4.82; N 10.57.

X-ray Structural Investigation. Crystals of the 1-ethylpyrazoloquinoline **3** are triclinic (DMF), at 20ºC: *a* = 7.527(2), *b* = 9.596(3), *c* = 13.758(4) Å, α = 80.35(3), β = 83.91(2), γ = 79.20(2)º, *V* = 959.5(5), Å^3, M_r = 397.44, *Z* = 2, space group $P\bar{1}$, d_{calc} = 1.376 g/cm^3, μ(MoKα) = 0.201 mm^{-1}, *F*(000) = 416. The unit cell parameters and intensities of 6349 reflections (3313 independent with R_{int} = 0.028) were measured on an Xcalibur-3 diffractometer (MoKα radiation, CCD detector, graphite monochromator, ω-scanning to $2\theta_{max}$ = 50º).

The structure was solved by a direct method using the SHELXTL program package [12]. The positions 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 = 0.073 for 3266 reflections (R_1 = 0.033 for 2087 reflections with $F > 4\sigma(F)$, *S* = 0.864).

The full crystallographic information has been placed in the Cambridge structural data bank (reference CCDC 672205). Interatomic distances and valence angles are given in Tables 2 and 3.

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