FORMATION OF A 4-QUINAZOLONE ON ATTEMPTING TO SYNTHESIZE A SYMMETRICAL AMIDINE OF ANTHRANILONITRILE.
# CRYSTAL STRUCTURE OF 3-(2-CYANOPHENYL)-4-QUINAZOLONE

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Attempts to synthesize a sym-diarylformamidine by the reaction of anthranilonitrile and its N-formyl derivative led to the formation of 3-(2-cyanophenyl)-4-quinazolone. The structure of the substance obtained was confirmed by x-ray analysis.

On the basis of the simple heteroalternation rule, a 5 + 1 scheme has been proposed for the synthesis of a series of pyridines and quinolines by the cyclization of a 1,5-biselectrophilic CCCNC fragment and a 1,1-bisnucleophilic one carbon fragment [1]. The predicted reaction scheme was confirmed experimentally [2] by the reaction of an anthranilic acid amidine [namely, 2-(N,N-dimethylaminomethyleneimino) benzoic acid] with nitromethane. Somewhat later an analogous 5 + 1 synthetic scheme (with the same distribution of polarity in the reactants) was rediscovered in the example of the reaction of N-trifluoroacetylanthranilic acid ester with a Wittig reagent [3].

Symmetrical amidines based on anthranilic acid derivatives are potential 1,5-biselectrophilic substrates useful for the synthesis of quinolines by this means. Either of the residues of the anthranilic acid derivative might emerge as leaving group in the reaction with a carbon bisnucleophile. One of the methods of synthesis of symmetrical amidines of aromatic amines (such as diphenylformamidine [4]) includes the condensation of an appropriate formanilide and an aniline. Up to the present time, anthranilic acid derivatives have not been used as substrates for such a reaction although several unsymmetrical amidines have been described [2, 5].

We found that 3-(2-cyanophenyl)-4-quinazolone was formed on attempting to obtain a symmetrical formamidine using anthranilonitrile as the aromatic amine.
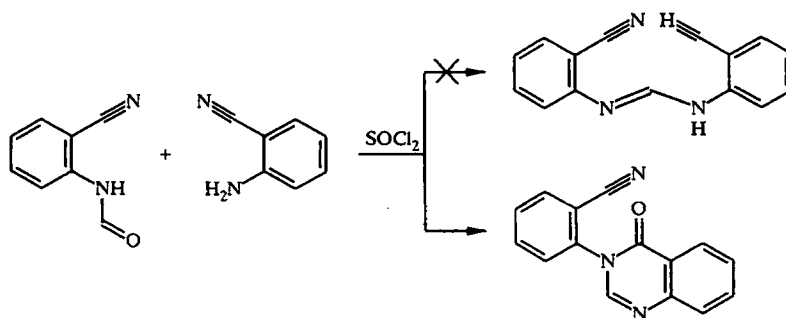
Assignment of the substance obtained as a 4-quinazolone was confirmed by IR spectral data, and the vibrational frequencies observed were typical of this class [6]. Peaks in the mass spectrum corresponded to the expected sequence of dissociation steps of the quinazolone fragment. The doublet in the PMR spectrum at 8.28 ppm was assigned probably to the

TABLE 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($U_{eq} \times 10^3$) in the Investigated Structure

| Atom	x	y	z	U_{eq}
$O_{(1)}$	−208(9)	1363(9)	3314(6)	54(2)
$N_{(1)}$	3037(11)	1304(9)	3280(7)	34(2)
$N_{(2)}$	2500(17)	4011(12)	893(10)	76(4)
$C_{(2)}$	4860(14)	1580(11)	3920(10)	40(3)
$N_{(3)}$	5280(12)	2368(9)	5068(8)	45(3)
$C_{(4)}$	3776(14)	2986(11)	5624(9)	38(3)
$C_{(5)}$	4235(16)	3919(13)	6800(10)	52(3)
$C_{(6)}$	2801(16)	4525(13)	7364(10)	54(3)
$C_{(7)}$	941(17)	4272(13)	6853(11)	61(4)
$C_{(8)}$	420(16)	3351(13)	5706(11)	57(4)
$C_{(9)}$	1865(15)	2702(11)	5090(10)	39(3)
$C_{(10)}$	1415(16)	1714(12)	3838(10)	37(3)
$C_{(11)}$	2833(14)	414(12)	2035(10)	37(3)
$C_{(12)}$	2557(14)	1122(13)	843(10)	38(3)
$C_{(13)}$	2340(14)	270(12)	−382(10)	41(3)
$C_{(14)}$	2392(14)	−1230(13)	−399(10)	44(3)
$C_{(15)}$	2618(15)	−1970(12)	746(11)	52(3)
$C_{(16)}$	2843(14)	−1138(13)	1998(10)	47(3)
$C_{(17)}$	2504(18)	2705(16)	857(11)	53(4)
$H_{(2)}$	5848	1183	3511	48
$H_{(5)}$	5492	4116	7183	62
$H_{(6)}$	3104	5149	8143	65
$H_{(7)}$	14	4725	7280	73
$H_{(8)}$	−853	3164	5352	68
$H_{(13)}$	2161	745	−1179	49
$H_{(14)}$	2271	−1785	−1219	52
$H_{(15)}$	2624	−3021	706	62
$H_{(16)}$	2996	−1635	2787	56
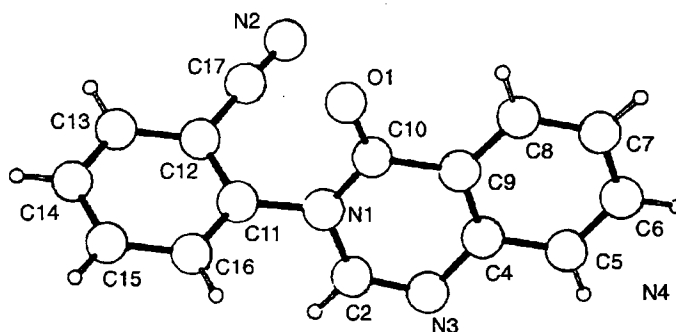
Fig. 1. Numbering of atoms in the structure of the investigated compound.

signal of the proton in the peri position to the 4-oxo group. Nevertheless the spectral methods did not permit a structure to be attributed unequivocally to the compound obtained. Final confirmation of the quinazolone structure was effected by x-ray analysis (see Fig. 1, Tables 1-3). As is evident, the aryl group (atoms $C_{(11)} - C_{(16)}$ in Fig. 1) in the structure of the compound obtained is turned relative to the $N_{(1)} - C_{(10)}$ fragment at the $N_{(1)} - C_{(11)}$ bond by 70°. The remaining geometrical parameters of the molecule (bond lengths and valence angles) are in good agreement with generally accepted values.

EXPERIMENTAL

3-(2-Cyanophenyl)-4-quinazolone. An excess of formic acid (54 mmole) was added to a solution of anthranilonitrile (5 mmole) in toluene (30 ml) and the mixture boiled for 2 h. The excess of formic acid and water were distilled off using a

TABLE 2. Bond Lengths d (Å) in the Investigated Compound

Bond	d	Bond	d
$O_{(1)}$—$C_{(10)}$	1,212(11)	$C_{(7)}$—$C_{(8)}$	1,376(13)
$N_{(1)}$—$C_{(10)}$	1,375(11)	$C_{(8)}$—$C_{(9)}$	1,400(12)
$N_{(1)}$—$C_{(2)}$	1,386(11)	$C_{(9)}$—$C_{(10)}$	1,486(12)
$N_{(1)}$—$C_{(11)}$	1,432(11)	$C_{(11)}$—$C_{(16)}$	1,373(12)
$N_{(2)}$—$C_{(17)}$	1,155(13)	$C(11)$—$C_{(12)}$	1,392(12)
$C_{(2)}$—$N_{(3)}$	1,312(11)	$C(12)$—$C_{(13)}$	1,399(12)
$N_{(3)}$—$C_{(4)}$	1,394(11)	$C(12)$—$C_{(17)}$	1,41(2)
$C_{(4)}$—$C_{(9)}$	1,397(12)	$C(13)$—$C_{(14)}$	1,335(12)
$C_{(4)}$—$C_{(5)}$	1,400(13)	$C(14)$—$C_{(15)}$	1,358(13)
$C_{(5)}$—$C_{(6)}$	1,351(13)	$C_{(15)}$—$C_{(16)}$	1,413(13)
$C_{(6)}$—$C_{(7)}$	1,357(14)		

TABLE 3. Valence Angles ω (deg) in the Investigated Compound

Angle	ω	Angle	w
$C_{(10)}$—$N_{(1)}$—$C_{(2)}$	123,3(8)	$O(1)$—$C_{(10)}$—$N_{(1)}$	122,7(9)
$C_{(10)}$—$N_{(1)}$—$C_{(11)}$	119,7(8)	$O(1)$—$C_{(10)}$—$C_{(9)}$	123,4(10)
$C_{(2)}$—$N_{(1)}$—$C_{(11)}$	116,7(8)	$N(1)$—$C_{(10)}$—$C_{(9)}$	113,7(10)
$N_{(3)}$—$C_{(2)}$—$N_{(1)}$	124,1(9)	$C(16)$—$C_{(11)}$—$C_{(12)}$	119,3(10)
$C_{(2)}$—$N_{(3)}$—$C_{(4)}$	116,0(9)	$C(16)$—$C_{(11)}$—$N_{(1)}$	121,4(10)
$N_{(3)}$—$C_{(4)}$—$C_{(9)}$	123,8(9)	$C(12)$—$C_{(11)}$—$N_{(1)}$	119,4(9)
$N_{(3)}$—$C_{(4)}$—$C_{(5)}$	117,0(10)	$C(11)$—$C_{(12)}$—$C_{(13)}$	120,3(10)
$C_{(9)}$—$C_{(4)}$—$C_{(5)}$	119,2(1)	$C(11)$—$C_{(12)}$—$C_{(17)}$	120,4(10)
$C_{(6)}$—$C_{(5)}$—$C_{(4)}$	118,2(10)	$C(13)$—$C_{(12)}$—$C_{(17)}$	119,3(10)
$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	123,5(11)	$C(14)$—$C_{(13)}$—$C_{(12)}$	119,5(10)
$C_{(6)}$—$C_{(7)}$—$C_{(8)}$	120,3(11)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	122,0(11)
$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	118,0(11)	$C_{(14)}$—$C_{(15)}$—$C_{(16)}$	119,8(10)
$C_{(4)}$—$C_{(9)}$—$C_{(8)}$	120,9(10)	$C(11)$—$C_{(16)}$—$C_{(15)}$	119,2(10)
$C_{(4)}$—$C_{(9)}$—$C_{(10)}$	118,2(10)	$N(2)$—$C_{(17)}$—$C_{(12)}$	178,2(14)
$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	120,9(10)		

Dean and Stark apparatus. Thionyl chloride (5 mmole) and anthranilonitrile (5 mmole) were added to the solution of N-formylanthranilonitrile obtained. The mixture was heated for 1 h and then evaporated in vacuum. The residue was treated with water. The aqueous solution contained unreacted N-formylanthranilonitrile. The insoluble residue (0.11 g, 9%, mp 191-192°C) was 3-(2-cyanophenyl)-4-quinazolone. IR spectrum (Nujol): 1617 (C=N), 1690 (C=O), 2247 cm^{-1} (CN). PMR spectrum (CD$_3$CN, 200 MHz): 8.28 (1H, d, J = 8 Hz, 5-H); 8.15 (1H, s, 2-H); 7.8 (7H, m, Ar). Mass spectrum, m/z (I, %); 247 (100) [M$^+$], 219 (91) [M$-$CO]$^+$, 192 (6) [M$-$CO$-$HCN]$^+$, 129 (20) [NCC$_6$H$_4$NCH]$^+$, 119 (16) [NCC$_6$H$_4$CO]$^+$, 102 (40) [C$_6$H$_4$CN]$^+$, 90 (20) [C$_6$H$_4$N]$^+$, 76 (25) [C$_6$H$_4$]$^+$.

The x-ray structural investigation of 3-(2-cyanophenyl)-4-quinazolone was carried out on a CAD-4 automatic monocrystal diffractometer using MoKα radiation. Unit cell parameters were determined and refined from 25 reflections in the θ angle range 12-13°. The crystals of the compound investigated were triclinic (space group P-1) with unit cell parameters a = 6.963(3), b = 8.845(9), c = 9.935(4) Å, α = 91.95(6)°, β = 90.09(6)°, γ = 103.30(6)°, Z = 2. The structure was solved by direct methods and refined by a full matrix least squares procedure with the SHELX [7] complex of programs in an anisotropic approach for the nonhydrogen atoms. The coordinates of hydrogen atoms were calculated from geometric considerations and refined to rigid binding with the corresponding carbon atoms. The final R factor was 8.81% from 1114 independent reflections with $I > 2\sigma$ (I).

The coordinates of atoms in the investigated compound and the isotropic thermal parameters equivalent to anisotropic are given in Table 1. The interatomic distances and the valence angles are given in Tables 2 and 3. The spatial disposition of atoms in the molecule and their numbering are shown in Fig. 1 [8].

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