Synthesis and structure of 6-chloro-2,3-trimethylene-4-phenylquinoline

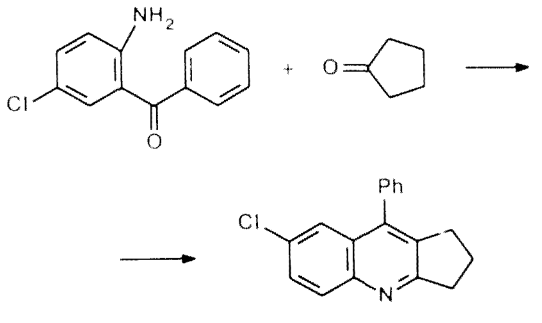
I. I. Ponomarev, O. V. Shishkin,* S. V. Lindeman, and Yu. V. Volkova

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085. E-mail: serg@xray.ineos.ac.ru

An X-ray structural investigation of 6-chloro-2,3-trimethylene-4-phenylquinoline obtained by the reaction of 2-amino-5-chlorobenzophenone with cyclopentanone was carried out. At 20 °C, a = 23.750, b = 9.242, c = 14.018 Å, β = 112.68°, space group $C2/c$, Z = 8, 2647 reflections, R = 0.047. The five-membered ring has an envelope conformation. Conjugation between the quinoline fragment and the phenyl substituent is significantly distorted due to the rotation of the latter by −62.9°.

Key words: 6-chloro-2,3-trimethylene-4-phenylquinoline, X-ray structural analysis, molecular structure.

In the last few years, the chemistry of heterocyclic polymers, which possess non-linear optical properties (NLO), has rapidly progressed.[1–3] Highly fused heterocyclic systems, which, in spite of their high values of the parameter χ^3, are strongly colored compounds and cannot be used in practice for optical devices, are of special interest. It this connection, it is necessary to use the Langmuir-Blodgett procedure for the preparation of NLO films[4] or to "dilute" a heterocyclic system with cycloaliphatic fragments, which are more transparent in the visible region.[1] In this regard, the reaction of *o*-aminobenzophenones with cycloaliphatic ketones found by us[5] is of significant interest and allows one to establish a correlation between the non-linear optical properties and the chemical composition and structures of model compounds. To extend our knowledge about the influence of composition and molecular structure on the NLO properties of a system, we have studied the reaction of 2-amino-5-cholorobenzophenone with cyclopentanone. As a result, 6-chloro-2,3-trimethylene-4-phenylquinoline (**1**) has been obtained, and X-ray structural analysis of this compound has been carried out. The reaction was carried out in triphenylphosphate (TPP) at 140 °C for 4 h.



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The X-ray structural analysis of compound **1** (Fig. 1, Tables 1–3) showed that the quinoline fragment of the molecule is planar. The five-membered ring has an envelope conformation. The C(9) atom is deflected by 0.21 Å from the least-square plane of the other atoms of the cycle. Non-valence interactions of the hydrogen atoms in the *ortho*-positions of the phenyl substituents with the hydrogen atoms at the C(4) and C(8) atoms (shortened intramolecular contact H(4)...C(14) 2.67(1) Å, the sum of van der Waals radii 2.78 Å)[6] result in rotation of the aromatic cycle by −62.9(3)° angle with respect to the quinoline fragment. The non-equivalence of these interactions for the two *ortho*-hydrogen atoms (interaction with the hydrogen atoms of

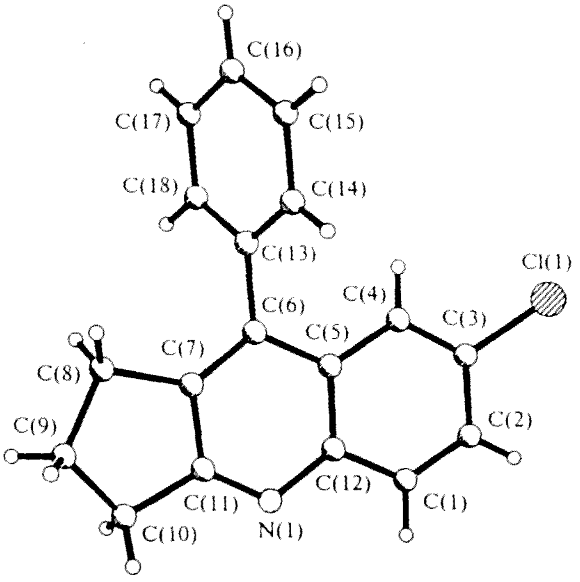

Fig. 1. Structure of molecule **1**.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1800–1802, July, 1996.

Table 1. Bond lengths (*d*) in structure **1**

Bond	*d*/Å	Bond	*d*/Å
Cl(1)—C(3)	1.742(3)	C(7)—C(11)	1.423(3)
N(1)—C(11)	1.302(3)	C(7)—C(8)	1.506(4)
N(1)—C(12)	1.369(3)	C(8)—C(9)	1.509(5)
C(1)—C(2)	1.350(4)	C(9)—C(10)	1.504(5)
C(1)—C(12)	1.416(4)	C(10)—C(11)	1.507(4)
C(2)—C(3)	1.399(4)	C(13)—C(14)	1.388(3)
C(3)—C(4)	1.356(3)	C(13)—C(18)	1.389(3)
C(4)—C(5)	1.407(3)	C(14)—C(15)	1.386(4)
C(5)—C(12)	1.424(3)	C(15)—C(16)	1.371(4)
C(5)—C(6)	1.437(3)	C(16)—C(17)	1.380(4)
C(6)—C(7)	1.359(3)	C(17)—C(18)	1.383(3)
C(6)—C(13)	1.490(3)		

Table 2. Bond angles (ω) in structure **1**

Angle	ω/deg	Angle	ω/deg
C(11)—N(1)—C(12)	116.6(2)	C(10)—C(9)—C(8)	109.6(3)
C(2)—C(1)—C(12)	122.1(2)	C(9)—C(10)—C(11)	104.2(2)
C(1)—C(2)—C(3)	118.8(2)	N(1)—C(11)—C(7)	125.1(2)
C(4)—C(3)—C(2)	121.7(2)	N(1)—C(11)—C(10)	125.0(2)
C(4)—C(3)—Cl(1)	120.1(2)	C(7)—C(11)—C(10)	110.0(2)
C(2)—C(3)—Cl(1)	118.2(2)	N(1)—C(12)—C(1)	118.7(2)
C(3)—C(4)—C(5)	120.8(2)	N(1)—C(12)—C(5)	123.0(2)
C(4)—C(5)—C(12)	118.3(2)	C(1)—C(12)—C(5)	118.3(2)
C(4)—C(5)—C(6)	123.5(2)	C(14)—C(13)—C(18)	118.9(2)
C(12)—C(5)—C(6)	118.3(2)	C(14)—C(13)—C(6)	120.7(2)
C(7)—C(6)—C(5)	117.2(2)	C(18)—C(13)—C(6)	120.4(2)
C(7)—C(6)—C(13)	122.3(2)	C(13)—C(14)—C(15)	120.6(2)
C(5)—C(6)—C(13)	120.5(2)	C(16)—C(15)—C(14)	120.0(3)
C(6)—C(7)—C(11)	119.9(2)	C(15)—C(16)—C(17)	120.1(2)
C(6)—C(7)—C(8)	129.7(2)	C(16)—C(17)—C(18)	120.2(2)
C(11)—C(7)—C(8)	110.3(2)	C(17)—C(18)—C(13)	120.2(2)
C(7)—C(8)—C(9)	103.9(3)		

Table 3. Selected torsion angles (φ) in structure **1**

Angle	φ/deg
C(11)−C(7)−C(8)−C(9)	8.1(4)
C(7)−C(8)−C(9)−C(10)	−13.7(5)
C(8)−C(9)−C(10)−C(11)	13.9(5)
C(8)−C(7)−C(11)−C(10)	0.4(3)
C(9)−C(10)−C(11)−C(7)	−8.7(4)
C(7)−C(6)−C(13)−C(18)	−62.9(3)

Table 4. Coordinates of non-hydrogen (×10^4) and hydrogen (×10^3) atoms in structure **1**

Atom	*x*	*y*	*z*
Cl(1)	−11(1)	3915(1)	1076(1)
N(1)	−2561(1)	5002(2)	517(2)
C(1)	−1801(2)	3601(3)	201(2)
C(2)	−1218(1)	3329(3)	325(2)
C(3)	−762(1)	4300(2)	902(2)
C(4)	−891(1)	5499(2)	1338(2)
C(5)	−1491(1)	5788(2)	1248(2)
C(6)	−1656(1)	7026(2)	1705(2)
C(7)	−2254(1)	7175(2)	1550(2)
C(8)	−2560(1)	8305(4)	1959(3)
C(9)	−3197(2)	7722(5)	1687(4)
C(10)	−3311(1)	6505(4)	924(3)
C(11)	−2687(1)	6130(3)	955(2)
C(12)	−1962(1)	4816(3)	658(2)
C(13)	−1182(1)	8077(2)	2330(2)
C(14)	−705(1)	7639(3)	3226(2)
C(15)	−260(1)	8615(3)	3799(2)
C(16)	−291(1)	10027(3)	3485(2)
C(17)	−763(1)	10479(3)	2597(2)
C(18)	−1207(1)	9510(2)	2018(2)
H(1)	−213(2)	296(4)	−19(3)
H(2)	−113(1)	252(3)	1(2)
H(4)	−58(1)	609(3)	171(2)
H(8A)	−258(2)	918(4)	163(3)
H(8B)	−232(2)	847(4)	272(3)
H(9A)	−324(2)	737(5)	231(3)
H(9B)	−349(2)	849(5)	139(3)
H(10A)	−347(2)	567(4)	114(3)
H(10B)	−357(2)	683(4)	20(3)
H(14)	−68(1)	673(4)	347(2)
H(15)	5(1)	826(4)	441(3)
H(16)	0(1)	1070(4)	386(2)
H(17)	−77(1)	1143(3)	240(2)
H(18)	−155(1)	983(3)	139(2)

the methylene group in one case and with the aromatic hydrogen atoms in the other) probably causes deformation of the bond angles at the C(6) atom (C(7)—C(6)—C(13) 122.3(2)°, C(5)—C(6)—C(13) 120.5(2)°).

The molecules in the crystals are packed at normal van der Waals distances without any specifc peculiarities.

Experimental

6-Chloro-2,3-trimethylene-4-phenylquinoline (**1**) was synthesized by a procedure similar to that described in Ref. 5. A mixture of 2-amino-5-chlorobenzophenone (0.46 g, 0.002 mol), cyclopentanone (0.4 g, 0.002 mol), and TPP (0.8 g) was heated in a flow of argon for 4 h at 130 °C. The mixture was then cooled and poured into a mixture of MeOH (4 mL) and triethylamine (1 mL). The crystals of **1** that precipitated were filtered off and purified by crystallization from MeOH to afford **1** in 97 % yield, m.p. 95—96 °C. Found (%): C, 77.20; H, 5.25; N, 4.98. $C_{18}H_{14}ClN$. Calculated (%): C, 77.27; H, 5.05; N, 5.01.

The crystals of **1** ($C_{18}H_{14}NCl$) are monoclinic. At 20 °C, a = 23.750(11), b = 9.242(5), c = 14.018(7) Å, β = 112.68(4)°, V = 2839(2) Å^3, d_{calc} = 1.309 g cm^{-3}, space group *C*2/*c*, Z = 8. Unit cell parameters and intensities of 3112 independent reflections (R_{int}= 0.03) were measured on a Siemens P3/PC automatic diffractometer (λMoKα, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 56°).

The structure was solved by the direct method using the SHELXTL PLUS program package.[7] Positions of hydrogen atoms were determined from differential maps of electron density.

The refinement against F^2 using the full-matrix least square method in the anisotropic (isotropic for hydrogen atoms) approximation for 2647 reflections was carried out to

$wR_2 = 0.189$ ($R_1 = 0.047$ for 2019 reflections with $F > 4\sigma(F)$, $S = 1.12$). The atomic coordinates are given in Table 4.

References

1. P. N. Prasad and D. J. Williams, *Introduction to Non-Linear Optical Effects in Molecules and Polymers*, Wiley Interscience, 1990.
2. A. K. Agrawal and S. A. Jenekhe, *Macromolecules*, 1993, **26**, 895.
3. B. A. Reinhardt, *TRIP*, 1993, **1**, 4.
4. V. V. Tsukruk, V. N. Bliznuyk, D. M. Visser, and I. I. Ponomarev, *ACS Polymer Preprints*, 1995, **36**, 83.
5. I. I. Ponomarev, O. V. Shishkin, S. V. Lindeman, and Yu. A. Volkova, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1467 [*Russ. Chem. Bull.*, 1994, **43**, 1390 (Engl. Transl.)].
6. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1989, **58**, 713 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
7. *SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data*. Rev. 5.03, Siemens Analytical X-Ray Instruments Inc., 1994.

Received January 22, 1996;
in revised form February 16, 1996