Synthesis and X-ray structural investigation of 6-chloro-10-phenyl-1,2,3,4-tetrahydroacridine

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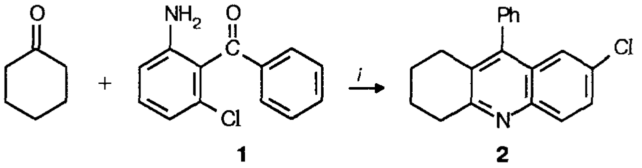
An X-ray structural study of 6-chloro-10-phenyl-1,2,3,4-tetrahydroacridine prepared by the reaction of cyclohexanone with 2-amino-5-chlorobenzofenone was carried out. At 20°C $a = 24.215(6)$, $b = 8.967(2)$, $c = 15.006(3)$ Å, $\beta = 115.57(2)°$, $V = 2939(1)$ Å^3, $d_{calc} = 1.310$ g cm^{-3}, $Z = 4$, space group $C2/c$, 1324 reflections, λMo$K\alpha$, $R = 0.038$. The cyclohexene ring has a half-chair conformation. The phenyl substituent is rotated 71.2° with respect to the plane of the quinoline fragment.

Key words: 6-chloro-10-phenyl-1,2,3,4-tetrahydroacridine, molecular structure, X-ray structural analysis.

Some fused heterocyclic systems are known to possess nonlinear optical properties,[1—3] high thermal characteristics, and interesting thermal properties. The reaction of cyclohexanone with 2-amino-5-chlorobenzophenone (**1**) found by us, which takes place in triphenyl phosphate (TPP) at 120 °C over a period of 4 h with nearly quantitative yield, is very promising for the preparation of these compounds.



i. TPP, 120°C

In the present work we carried out an X-ray structural study of the product of this reaction, 6-chloro-10-phenyl-1,2,3,4-terahydroacridine (**2**) (Fig. 1, Table 1).

The partially hydrogenated ring in molecule **2** has a half-chair conformation. The C(11) and C(12) atoms are deflected from the root-mean-square plane, C(8)C(9)C(10)C(13), in opposite directions by 0.35 and −0.42 Å, respectively. The phenyl substituent at C(7) is rotated with respect to the plane of the quinoline ring by 71.2(4)°; this results in the disturbance of the conjugation between the π-electronic systems of these moieties.

The X-ray structural study confirmed the unstrained fused structure of compound **2**, which suggests the possibility of synthesizing ladder-type polyheteroarylenes starting from bis-cyclohexanones (for example, 1,4-cyclohexanediones) and bis-(*o*-aminobenzophenones) (for example, 1,5-diamino-2,4-dibenzoylbenzenes).

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

C(5)—N—C(9)	118.3(2)	C(2)—C(1)—C(6)	119.7(2)
Cl—C(2)—C(1)	119.1(2)	Cl—C(2)—C(3)	118.6(2)
C(1)—C(2)—C(3)	122.3(3)	C(2)—C(3)—C(4)	119.2(3)
C(3)—C(4)—C(5)	120.8(2)	N—C(5)—C(4)	118.1(2)
N—C(5)—C(6)	122.6(2)	C(4)—C(5)—C(6)	119.4(3)
C(1)—C(6)—C(5)	118.6(2)	C(1)—C(6)—C(7)	123.4(2)
C(5)—C(6)—C(7)	117.9(2)	C(9)—C(8)—C(7)	118.6(2)
C(9)—C(8)—C(13)	120.3(2)	C(7)—C(8)—C(13)	121.1(2)
N—C(9)—C(8)	123.6(3)	N—C(9)—C(10)	115.8(2)
C(8)—C(9)—C(10)	120.6(3)	C(6)—C(7)—C(8)	118.9(2)
C(6)—C(7)—C(14)	119.3(2)	C(8)—C(7)—C(14)	121.8(2)
C(9)—C(10)—C(11)	114.7(2)	C(10)—C(11)—C(12)	109.9(2)
C(11)—C(12)—C(13)	109.7(3)	C(8)—C(13)—C(12)	114.1(2)
C(7)—C(14)—C(15)	120.8(2)	C(7)—C(14)—C(19)	120.7(2)
C(15)—C(14)—C(19)	118.4(2)	C(14)—C(15)—C(16)	120.6(2)
C(15)—C(16)—C(17)	120.4(3)	C(16)—C(17)—C(18)	119.9(3)
C(17)—C(18)—C(19)	120.4(2)	C(14)—C(19)—C(18)	120.3(3)

Experimental

2-Amino-5-chlorobenzophenone (1) from Fluka, m.p. 96—98 °C; triphenyl phosphate of the 'pure' grade, m.p. 50—52 °C; and cyclohexanone of the 'pure' grade, b.p. 155 °C, were used without further purification.

Preparation of 6-chloro-10-phenyl-1,2,3,4-tetrahydroacridine (2). Compound **1** (0.464 g, 0.002 mol L^{-1}), cyclohexanone (0.3 mL, 0.0028 mol L^{-1}), and TPP (0.5 g) were placed into a flask equipped with an argon inlet tube and

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Table 2. Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in structure **2**

Atom	x	y	z
Cl	98(1)	1028(1)	3914(1)
N	2636(1)	−113(2)	4591(1)
C(1)	954(1)	−529(3)	3645(2)
C(2)	846(1)	646(3)	4110(2)
C(3)	1314(1)	1561(3)	4752(2)
C(4)	1901(1)	1264(3)	4922(2)
C(5)	2038(1)	76(3)	4432(2)
C(6)	1561(1)	−839(3)	3787(2)
C(7)	1713(1)	−2009(3)	3292(2)
C(8)	2314(1)	−2161(3)	3435(2)
C(9)	2762(1)	−1179(3)	4108(2)
C(10)	3419(1)	−1280(3)	4273(2)
C(11)	3583(1)	−2695(3)	3902(2)
C(12)	3101(1)	−3038(3)	2868(2)
C(13)	2493(1)	−3324(3)	2892(2)
C(14)	1224(1)	−3030(3)	2637(2)
C(15)	1186(1)	−4478(3)	2926(2)
C(16)	713(1)	−5391(3)	2342(2)
C(17)	274(1)	−4886(3)	1459(2)
C(18)	307(1)	−3471(4)	1156(2)
C(19)	781(1)	−2538(3)	1737(2)
H(1)	64(1)	−114(1)	324(1)
H(3)	121(1)	238(1)	504(1)
H(4)	223(1)	190(1)	535(1)
H(10A)	354(1)	−37(1)	397(1)
H(10B)	365(1)	−111(1)	491(1)
H(11A)	397(1)	−257(1)	397(1)
H(11B)	357(1)	−369(1)	434(1)
H(12A)	307(1)	−215(1)	243(1)
H(12B)	330(1)	−389(1)	266(1)
H(13A)	219(1)	−349(1)	222(1)
H(13B)	249(1)	−432(1)	318(1)
H(15)	147(1)	−480(1)	351(1)
H(16)	71(1)	−640(1)	251(1)
H(17)	−7(1)	−555(1)	105(1)
H(18)	2(1)	−305(1)	53(1)
H(19)	78(1)	−161(1)	151(1)

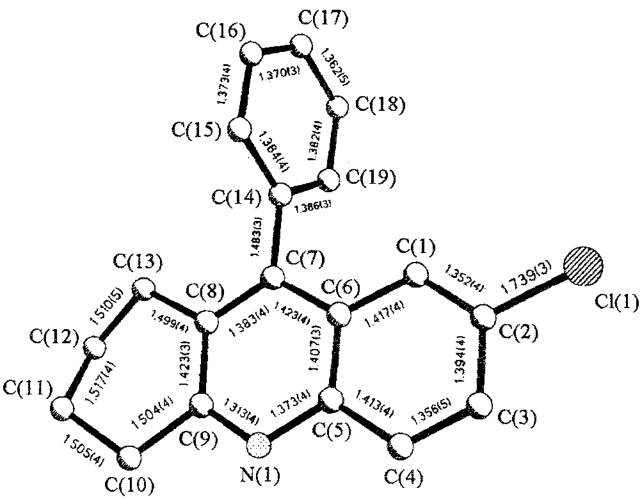

Fig. 1. The structure of molecule **2**. H atoms are not shown.

a stirrer, and the mixture was heated at 140 °C for 4 h in an argon flow and cooled. A mixture of EtOH (10 mL) and triethylamine (1 mL) was added. The crystals that precipitated on cooling in a refrigerator were filtered off, washed with EtOH on the filter, and dried. Yield 0.59 g. Found (%): C, 77.29; H, 5.90; N, 4.69. $C_{19}H_{17}ClN$, M_r = 294.85. Calculated (%): C, 77.40; H, 5.81; N,4.75.

The X-ray structural study. The crystals of **2** prepared by slow sublimation at 140 °C *in vacuo* were monoclinic. At 20 °C a = 24.215(6), b = 8.967(2), c = 15.006(3) Å, β = 115.57(2)°, V = 2939(1) Å^3, d_{calc} = 1.310 g cm^{-3}, Z = 4, space group $C2/c$. Unit cell parameters and intensities of 1324 reflections with $F > 6\sigma(F)$ were measured on a Syntex P2_1 automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$-scanning, $2\theta_{max}$ = 60°).

The structure was solved by the direct method using the SHELXTL PLUS set of programs. Positions of the H atoms were found from the differential synthesis of the electron density. The refinement was carried out by the full-matrix least-squares method in the anisotropic approximation (in the isotropic approximation for H atoms) to R = 0.038 (R_w = 0.045, S = 1.56). The atomic coordinates are listed in Table 2. The bond lengths are presented in Fig. 1.

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