Crystal Structures of Two 2-Substituted 8-Quinolinols

Chitoshi KITAMURA,^{*,†} Jun-Ichi TANAKA,^{*} Shin-ichi OHFUCHI,^{**} and Akio YONEDA^{*}

^{*}Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

^{**}Department of Applied Chemistry, Kobe City College of Technology, Nishi-ku, Kobe, Hyogo 651-2194

The title compound, 2-(2-cyano-2-ethoxycarbonyl-ethyl)-8-quinolinol (I), $C_{15}H_{14}N_2O_3$, crystallizes in the triclinic system, space group $P\bar{1}$ with cell constants: $a = 5.9476(5)$, $b = 9.9004(5)$, $c = 12.3459(4)$ Å, $\alpha = 68.468(9)$, $\beta = 82.168(14)$, $\gamma = 89.144(15)^\circ$, $V = 669.44(7)$ Å³, $Z = 2$. 2-(2,2-Dicyanovinyl)-8-quinolinol (II), $C_{13}H_7N_3O$, crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 7.040(4)$, $b = 8.131(5)$, $c = 10.198(5)$ Å, $\alpha = 97.01(2)$, $\beta = 108.93(3)$, $\gamma = 102.45(2)^\circ$, $V = 527.4(5)$ Å³, $Z = 2$. The structure of II adopts a planar conformation.

(Received August 8, 2007; Accepted September 26, 2007; Published on web November 29, 2007)

2-Substituted 8-quinolinols containing C, N and O donor sites can form Pd complexes having a Pd-C(sp³) single bond in the presence of an amine external ligand.¹ We recently synthesized new 2-substituted 8-quinolinols, and have been searching for a relationship between the complexation of the quinolinols and the acidity in the OH group. We here report on the crystal structures of two new 2-substituted 8-quinolinols, 2-(2-cyano-2-ethoxycarbonyl-ethyl)-8-quinolinol (I) and 2-(2,2-dicyanovinyl)-8-quinolinol (II).

The syntheses of I and II were performed by a previously reported method.¹ Single crystals were obtained by slow evaporation from chloroform solutions. X-ray data were collected using a Rigaku/MSC Mercury CCD diffractometer using graphite-monochromated Mo- K_α ($\alpha = 0.71070$ Å) radiation at 223 K. The structure was solved by a direct method using SIR2004.² All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.³ The positions of the hydrogen atoms were obtained from a difference Fourier map, and the hydrogen atoms were included in the refinement using the riding model. All calculations were performed using the WinGX program package.⁴ Crystal and experimental data are listed in Table 1. The final positional parameters are given in Table 2. The molecular structures of I and II are depicted in Figs. 2 and 3, respectively. The bond lengths and bond angles are all within the expected ranges.

In I, C11 atom deviates by 0.434 Å from the quinoline plane, although the C10 atom lies in the plane. The torsion angle of N1-C1-C10-C11 is 17.15(15)°. The cyano and ethoxycarbonyl

groups are extended out of the quinoline plane. Thus, the torsion angles of C1-C10-C11-C12 and C1-C10-C11-C13 are 67.32(13) and -57.30(13)°, respectively. There is an intermolecular C-H...O hydrogen bond between the C11 and O3 atoms [C11...O3 (-x+1, -y+1, -z+1) 3.397(2), C11-H 0.99, H...O3 (-x+1, -y+1, -z+1) 2.525(1) Å, C11-H...O3 (-x+1, -y+1, -z+1) 146.72(7)°]. The two intermolecular C-H...O hydrogen bonds between the C11 and O3 atoms form a dimer pair of I around the inversion center in the unit cell. In II, the molecule has an almost planar conformation. The torsion angle of

Table 1 Crystal and experimental data

	I	II
Formula	$C_{15}H_{14}N_2O_3$	$C_{13}H_7N_3O$
Formula weight	270.28	221.22
Crystal color, habit	colorless, prism	yellow, platelet
Crystal size/mm	0.50 × 0.20 × 0.10	0.30 × 0.30 × 0.10
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temperature/K	223	223
Z	2	2
a/Å	5.9476(5)	7.040(4)
b/Å	9.9004(5)	8.131(5)
c/Å	12.3459(4)	10.198(5)
α /deg	68.468(9)	97.01(2)
β /deg	82.168(14)	108.93(3)
γ /deg	89.144(15)	102.45(2)
V/Å ³	669.44(7)	527.4(5)
$D_{\text{calc}}/\text{g cm}^{-3}$	1.341	1.393
No. of reflections [$I > 2\sigma(I)$]	2701	2140
$2\theta_{\text{max}}/^\circ$ with Mo K_α	55.0	55.0
R, R_w [$I > 2\sigma(I)$]	0.0445, 0.1066	0.0530, 0.1269
$(\Delta/\sigma)_{\text{max}}$	0.000	0.000
$(\Delta\rho)_{\text{max}}/\text{e Å}^{-3}$	0.234	0.200
$(\Delta\rho)_{\text{min}}/\text{e Å}^{-3}$	-0.138	-0.173
Measurement	Rigaku/MSC Mercury CCD	
Program system	WinGX	
Structure determination	direct methods (SIR2004)	
Refinement	full-matrix least-squares on F^2 (SHELXL97)	
CCDC	653954	653955

Fig. 1 Chemical structure of 2-(2-cyano-2-ethoxycarbonyl-ethyl)-8-quinolinol (I) and 2-(2,2-dicyanovinyl)-8-quinolinol (II).

[†] To whom correspondence should be addressed.
E-mail: kitamura@eng.u-hyogo.ac.jp

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
I				
C(1)	4722(2)	5646(1)	7803(1)	31(1)
C(2)	2964(2)	5580(2)	8725(1)	41(1)
C(3)	3177(2)	6395(2)	9384(1)	44(1)
C(4)	5134(2)	7301(1)	9155(1)	37(1)
C(5)	5546(3)	8168(2)	9804(1)	47(1)
C(6)	7504(3)	8993(2)	9512(1)	51(1)
C(7)	9138(3)	9032(2)	8566(1)	45(1)
C(8)	8784(2)	8211(1)	7916(1)	35(1)
C(9)	6788(2)	7311(1)	8212(1)	30(1)
C(10)	4533(2)	4764(1)	7053(1)	34(1)
C(11)	6821(2)	4632(1)	6353(1)	29(1)
C(12)	8371(2)	3763(1)	7149(1)	31(1)
C(13)	7968(2)	6091(1)	5554(1)	28(1)
C(14)	7201(2)	8429(1)	4230(1)	44(1)
C(15)	5221(3)	9165(2)	3669(2)	72(1)
N(1)	6564(2)	6484(1)	7557(1)	29(1)
N(2)	9474(2)	3033(1)	7799(1)	44(1)
O(1)	10336(2)	8255(1)	6985(1)	44(1)
O(2)	9955(1)	6415(1)	5448(1)	34(1)
O(3)	6456(1)	6930(1)	4948(1)	35(1)
II				
C(1)	2823(2)	1678(2)	958(1)	28(1)
C(2)	2886(2)	2645(2)	-96(2)	35(1)
C(3)	2642(2)	1818(2)	-1408(2)	37(1)
C(4)	2322(2)	20(2)	-1701(1)	32(1)
C(5)	2037(2)	-967(2)	-3025(2)	43(1)
C(6)	1715(2)	-2708(2)	-3197(2)	50(1)
C(7)	1654(2)	-3565(2)	-2096(2)	49(1)
C(8)	1957(2)	-2645(2)	-787(2)	37(1)
C(9)	2282(2)	-832(2)	-574(1)	29(1)
C(10)	3083(2)	2549(2)	2364(1)	30(1)
C(11)	3066(2)	1804(2)	3471(1)	31(1)
C(12)	2779(2)	-4(2)	3459(1)	35(1)
C(13)	3318(2)	2842(2)	4795(1)	37(1)
N(1)	2533(2)	-11(1)	730(1)	27(1)
N(2)	2550(2)	-1413(2)	3565(2)	51(1)
N(3)	3488(2)	3656(2)	5841(1)	49(1)
O(1)	1975(2)	3420(1)	316(1)	50(1)

N1-C1-C10-C11 is $17.15(15)^\circ$. The terminal N2 and N3 atoms are coplanar to a quinoline plane within $0.006 \text{ \AA}$. There is an intermolecular C-H...N hydrogen bond between the C10 and N3 atoms [C10...N3 ($-x+1, -y+1, -z+1$) $3.353(2)$, C10-H 0.94 , H...N3 ($-x+1, -y+1, -z+1$) $2.652(1) \text{ \AA}$, C10-H-N3 ($-x+1, -y+1, -z+1$) $131.89(10)^\circ$]. Similarly to I, II shows that the two intermolecular C-H...N hydrogen bonds between the C10 and N3 atoms make a dimer pair of II around the inversion center in the unit cell. In both I and II, the 8-quinolinol moieties form face-to-face slipped π -stacks. The interplanar distances between overlapping 8-quinolinol moieties in I and II are $3.329(2)$ and $3.420(2) \text{ \AA}$, respectively. In the formation of cyclometalated Pd(II) complexes,¹ the C11 atoms of I and II act as a donor and construct a stable Pd-C single bond. It is shown

Fig. 2 ORTEP drawing of compound I with atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

Fig. 3 ORTEP drawing of compound II with atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

that the C11 atoms lie at the correct place to form the Pd-C bond.

Acknowledgements

We thank the Research Center for the Instrument Center, the Institute for Molecular Science, for assistance in obtaining X-ray data.

References

1. A. Yoneda, G. R. Newkome, and K. J. Theriot, *J. Organomet. Chem.*, **1991**, 401, 217.
2. M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, and R. Spagana, *J. Appl. Cryst.*, **2005**, 38, 381.
3. G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, **1997**.
4. L. J. Farrugia, *J. Appl. Cryst.*, **1999**, 32, 837.