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# Revision of the Assigned Structures of 5- and 7-Iodo-8-quinolinols and 5- and 7-Iodo-2-methyl-8-quinolinols

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**Summary.** Revised structures are presented for 5- and 7-iodo-8-quinolinols and for 5- and 7-iodo-2-methyl-8-quinolinols based on NMR studies. UV spectroscopic characterization of the compounds was also carried out.

**Keywords**. 5-Iodo-8-quinolinol; 7-Iodo-8-quinolinol; 5-Iodo-2-methyl-8-quinolinol; 7-Iodo-2-methyl-8-quinolinol; $^1$H NMR; $^{13}$C NMR; UV spectra.

### Berichtigung der Strukturen von 5- und 7-Iod-8-chinolinolen sowie von 5- und 7-Iod-2-methyl-8-chinolinolen

**Zusammenfassung.** Eine Richtigstellung der publizierten Strukturen von 5- und 7-Iod-8-chinolinolen sowie von 5- und 7-Iod-2-methyl-8-chinolinolen wird präsentiert. Als Grundlage der Neuzuordnung dienen NMR- und UV-Untersuchungen.

## Introduction

Whereas 5,7-diiodo-8-quinolinol was described in 1898 [1], monoiodo-8-quinolinol (m.p.: 127–128°C) was first reported by *Matsumura* in 1927 [2]. It was stated that the position of the iodine atom was not proved, but by analogy with the chloro and bromo derivatives, it seemed highly probable that it was in position 5. This has been accepted until now. A 1995 report described a monoiodo-8-quinolinol (m.p.: 135°C) prepared by a procedure similar to *Matsumura*'s as a new compound called 7-iodo-8-quinolinol [3]. This was based on a $^1$H decoupled $^{13}$C NMR spectrum. By additivity rules, the $^{13}$C NMR spectrum of "5-iodo-8-quinolinol" [2] seemed to fit the new assignment. Also, its $^1$H coupled $^{13}$C NMR spectrum where $^3J_{CH}$ can be seen, didn't match with that of authentic 5-chloro and 5-bromo-8-quinolinols. The latter matched the accepted "7-iodo-8-quinolinol" (m.p.: 112–113°C) [4]. An X-ray crystal structure determination confirmed that the monoiodo-8-quinolinol (m.p.: 127–128°C) [2] is in fact 7-iodo-8-quinolinol [5]. Thus, the previously accepted "7-iodo-8-quinolinol" [4] needed to have its structure

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reexamined. Since the monoiodo-2-methyl-8-quinolinols [6, 7] were prepared by methods analogous to those above, their structures were reviewed also.

## Results and Discussion

For 8-quinolinol, $\delta$ of C-7 (111.2 ppm) has a lower value than $\delta$ of C-5 (117.8 ppm). It is predicted that by adding the substituent constant $Z$ for iodine on an aromatic ring [8], $\delta$ of C-7 in 7-iodo-8-quinolinol ($111.2–32.3 = 78.9$ ppm) $< \delta$ of C-5 in 5-iodo-8-quinolinol ($117.8–32.3 = 85.5$ ppm). The chemical shifts found using our samples labeled "7-iodo-8-quinolinol" (83.3 ppm) and "5-iodo-8-quinolinol" (78.9 ppm) showed the reverse behavior indicating that these structures had been misassigned (Table 1).

$^{1}$H coupled $^{13}$C NMR spectra of these substances confirmed that the names must be reversed. On a benzene ring, $^{3}J_{\mathrm{CH}} > {}^{2}J_{\mathrm{CH}} > {}^{4}J_{\mathrm{CH}}$, and at the usual resolution only $^{3}J_{\mathrm{CH}}$ (5–10 Hz) is observable, usually in addition to $^{1}J_{\mathrm{CH}}$ ($\sim$160 Hz) [8]. If no H is attached to a C atom *meta* to the one observed, it has no $^{3}J_{\mathrm{CH}}$, and its signals are much more intense than those of carbon atoms displaying a $^{3}J_{\mathrm{CH}}$. Thus, C-6 of 8-quinolinol is identified uniquely in its $^{1}$H coupled $^{13}$C NMR spectrum. For 5-halo derivatives of 8-quinolinol, both C-5 and C-6 are predicted to show this behavior. Authentic 5-chloro and 5-bromo-8-quinolinol behaved as predicted; "7-iodo-8-quinolinol" behaved like 5-chloro and 5-bromo-8-quinolinol in this type of experiment, proving conclusively that it is really 5-iodo-8-quinolinol. The sample labeled "5-iodo-8-quinolinol" lacked $^{3}J_{\mathrm{CH}}$ at C-6; so it must be 7-iodo-8-quinolinol. In this molecule, C-5 is split both by its attached H and the H at C-4 on the adjacent ring. The C bearing iodine (C-7) was a doublet for the sample of m.p. 127–128°C, whereas it was a triplet in that of the true 5-iodo-8-quinolinol (m.p. 112–113°C); in this case, long range splitting is caused by the protons attached to C-4 and C-7. Irradiating H-4 of " 5-iodo-8-quinolinol" [4] in a Nuclear *Overhauser* experiment led to strong polarization transfer to H-5 and to H-3 and H-2, showing all these Hs to be close in space as expected for the real 7-iodo-8-quinolinol.

**Table 1.** $^{13}$C chemical shifts ($\delta$, ppm) for 8-quinolinol, 2-methyl-8-quinolinol, and their 5- and 7-Iodo-derivatives

| Compound | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-8a | C-4a | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| *OX*[1] | 148.1 | 121.8 | 136.0 | 117.8 | 127.5 | 111.2 | 153.3 | 138.6 | 128.9 | – |
| 5-Iodo-*OX* | 148.6 | 123.4 | 139.3 | **83.3** | 137.8 | 112.9 | 154.1 | 141.0 | 129.7 | – |
| 7-Iodo-*OX* | 148.4 | 122.0 | 136.0 | 119.2 | 135.6 | **78.9** | 153.3 | 137.4 | 129.3 | – |
| 7-Iodo-*OX*[2] | 149.7 | 123.4 | 137.2[4] | 129.3[4] | 137.0 | **77.7** | 154.3 | 138.3 | 129.3[4] | – |
| 2-Methyl-*OX*[3] | 156.7 | 122.5 | 136.0 | 117.5 | 126.6 | 109.8 | 151.7 | 137.6 | 126.6 | 24.8 |
| 5-I-2-Me-*OX* | 157.4 | 124.1 | 139.2 | **83.2** | 136.6 | 112.6 | 153.2 | 138.5 | 127.9 | 23.9 |
| 7-I-2-Me-*OX* | 157.3 | 122.8 | 136.0 | 118.9 | 134.4 | **78.2** | 152.3 | 136.6 | 126.1 | 24.3 |

[1] *OX* = 8-quinolinol; data taken from Ref [9]; *DMSO*-$d_6$ as solvent in all cases unless otherwise stated; [2] data taken from Ref. [3], solvent *acetone*-$d_6$; [3] data taken from Aldrich Library of $^{13}$C and $^{1}$H NMR spectra, solvent $CDCl_3$; [4] the $\delta$ value for C-5 appears to be a misprint; apparently, it should be 119.3; the values for C-4 and C-4a are also interchanged from those described in Ref. [3]

**Table 2**. Comparison of proton chemical shifts ($\delta$, ppm) for 5-*X* and 7-*X-OX*

| | 5-*X-OX* | | | 7-*X-OX* | | |
|---|---|---|---|---|---|---|
| *X* | H-6 | H-7 | $\Delta\delta$ | H-5 | H-6 | $\Delta\delta$ |
| F | 7.19[1] | 7.01[1] | **0.18** | 7.36[2] | 7.38[2] | **0.02** |
| Cl | 7.64[1] | 7.18[1] | **0.46** | 7.46[3] | 7.56[3] | **0.10** |
| Br | 7.84[1] | 7.16[1] | **0.68** | 7.45[3] | 7.75[3] | **0.30** |
| I | 8.03[1] | 7.02[1] | **1.01** | 7.28[4] | 7.86[4] | **0.58** |
| H | 7.44[5] | 7.11[5] | **0.33** | 7.37[5] | 7.44[5] | **0.07** |
| $NH_2$ | 6.98[4] | 6.72[4] | **0.26** | 7.22[4] | 7.22[4] | **0.00** |
| $NO_2$ | 8.60[4] | 7.22[4] | **1.38** | 7.53[4] | 8.13[4] | **0.60** |

[1] Values reported here are *ca* 0.3 ppm greater than in Ref. [6]; apparently, zero was set on a spinning side band of *TMS*; [2] a sample prepared in Ref. [4] was used for these measurements; [3] these values agree with those in Ref. [11]; [4] these values agree with those in Ref. [4]; [5] values reported here agree with those in Ref. [10]

**Table 3**. Ultraviolet absorption spectroscopic data

| Compound | $\lambda_{max}$ (nm) | $\log \varepsilon$ |
|---|---|---|
| 8-quinolinol | 241.3±0.1 | 4.60±0.03 |
| 5-iodo-8-quinolinol | 248.0±0.1 | 4.49±0.03 |
| 7-iodo-8-quinolinol | 250.4±0.1 | 4.69±0.03 |
| 2-methyl-8-quinolinol | 243.4±0.1 | 4.62±0.03 |
| 5-iodo-2-methyl-8-quinolinol | 250.6±0.1 | 4.51±0.03 |
| 7-iodo-2-methyl-8-quinolinol | 252.0±0.1 | 4.73±0.03 |

Since the 2-methyl-monoiodo-8-quinolinols [6, 7] were prepared similarly to the monoiodo-8-quinolinols, they were expected to show the same need for correcting their structural assignments; the $^1$H coupled as well as $^1$H decoupled $^{13}$C NMR spectra confirmed this (Table 1). 5- and 7-substituted 8-quinolinols are distinguishable also by considering the difference in the chemical shifts of the A and B protons of the AB quartet due to the protons on the phenolic ring. $\Delta\delta$ in an isomeric pair is greater in the 5-substituted than in the 7-substituted compound (Table 2). UV absorption spectra for these compounds are given in Table 3. The absorption maximum is shifted to longer wavelengths on iodination, with substitution a C-7 causing a greater shift than substitution at C-5. It is also evident that molar absorptivities are lower than those of the parent compound for substitution at C-5, whereas they are higher for 7-substituted derivatives.

## Experimental

$^1$H and $^{13}$C NMR spectra were measured at 300 MHz and 75 MHz respectively on a Bruker Avance DPX-300 spectrometer using *DMSO*-$d_6$ as solvent; chemical shifts ($\delta$) are expressed in parts per million from *TMS* as internal standard. "5- and 7-iodo-8-quinolinols" and "2-methyl-5- and 7-iodo-8-quinolinols" have been described previously [4, 7]. Ultraviolet absorption spectra were measured on a Perkin Elmer Lambda 2 UV/Vis spectrophotometer using solutions dissolved in spectrophotometric grade methanol.

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