

Yoshihisa Kurasawa\*, Akiko Takano, and Kyoko Kato

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108, Japan

Ho Sik Kim

Department of Chemistry, Catholic University of Taegu-Hyosung, Gyongsan 713-702, Korea

Yoshihisa Okamoto

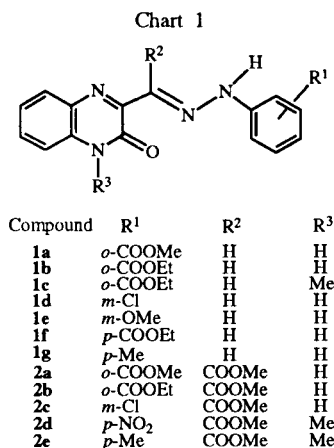
Division of Chemistry, College of Liberal Arts and Sciences, Kitasato University,  
Kitasato, Sagami-hara, Kanagawa 227, Japan

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The <sup>13</sup>C-nmr study was carried out for the tautomerism of the 3-(arylhydrazono)methyl-2-oxo-1,2-dihydroquinoxalines **1a-g** and **2a-e** between the hydrazone imine **A** and diazenylenamine **B** forms, providing the carbon chemical shifts for the tautomers **A** and **B** of compounds **1a-g** and **2a-e**. The comparison of the carbon chemical shifts for the tautomer **B** of compounds **1d**, **1f**, and **2b** in deuteriodimethyl sulfoxide with those in deuteriotrifluoroacetic acid showed that the C<sub>4a</sub>, C<sub>5</sub>, and diazenyl carbons were considerably shielded presumably due to the azo *N*-deuteration in deuteriotrifluoroacetic acid.

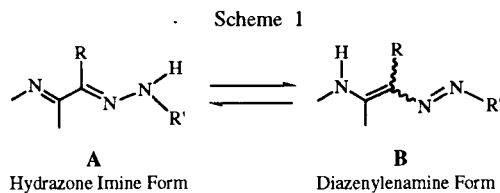
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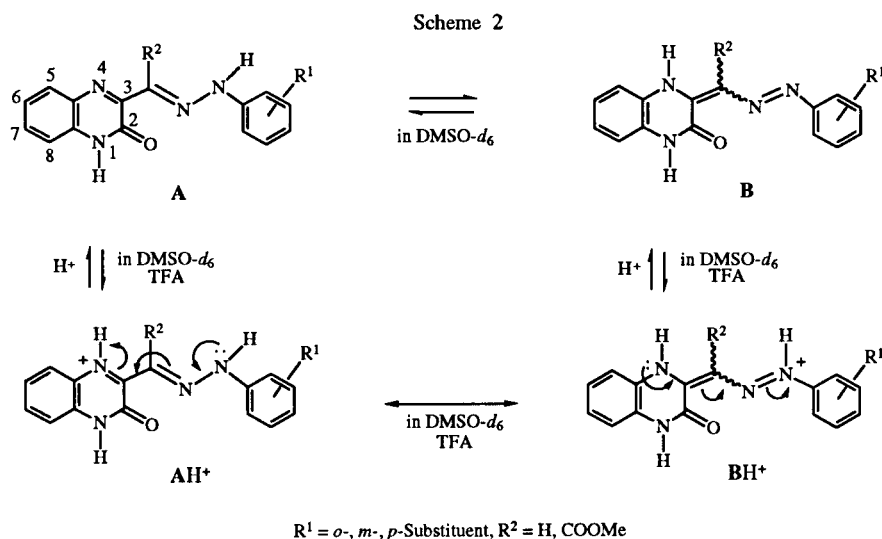
In previous papers [1-6], we reported that the <sup>1</sup>H-nmr spectra of the *o*-, *m*-, and *p*-substituted 3-(arylhydrazono)methyl-2-oxo-1,2-dihydroquinoxalines **1** and **2** (Chart 1) showed the evidence for the tautomeric equilib-



ria between the hydrazone imine **A** and diazenylenamine **B** forms in dimethyl sulfoxide or a series of mixed dimethyl sulfoxide/trifluoroacetic acid (Schemes 1, 2), and com-

pounds **1** and **2** existed as the diazenylenamine form **BH**<sup>+</sup> (Scheme 2) in trifluoroacetic acid [1-7]. Thereafter, we clarified that there was a correlation between the tautomeric equilibrium constants  $K_T$  ( $[A]/[B]$ ) and the Hammett  $\sigma_m$  and  $\sigma_p$  constants in the dimethyl sulfoxide media of the *m*- and *p*-substituted 3-(arylhydrazono)methyl-2-oxo-1,2-dihydroquinoxalines **1** [1-3]. Moreover, the classification of the chemical shifts due to the hydrazone NH and/or hydrazone CH protons (**A** form) and the N<sub>4</sub>-H and/or diazenyl CH protons (**B** form) in the dimethyl sulfoxide media of *o*-, *m*-, and *p*-substituted compounds **1** and **2** were found to be useful for the specification of the signals due to the hydrazone imine **A** and diazenylenamine **B** tautomers [7]. However, there have been few papers dealing with the <sup>13</sup>C-nmr study on the tautomerism of the *o*-, *m*-, and *p*-substituted compounds **1** and **2** between the **A** and **B** forms. Accordingly, we undertook the assignment of the carbon signals due to the tautomers **A** and **B** in the deuteriodimethyl sulfoxide or deuteriotrifluoroacetic acid media of compounds **1** and **2**. From these results, we further found that the C<sub>4a</sub>, C<sub>5</sub>, and diazenyl carbons of compounds **1** and **2** in deuteriotrifluoroacetic acid were eminently shielded when compared with those in deuteriodimethyl sulfoxide. This paper describes the carbon chemical shifts due to the tautomers **A** and **B** of compounds **1** and **2** in deuteriodimethyl sulfoxide or deuteriotrifluoroacetic acid together with the influence of the azo *N*-deuteration on the carbon chemical shifts.





In order to specify the carbon signals due to the hydrazone imine **A** and diazenylenamine **B** tautomers, the HMBC and HMQC spectra were measured for compounds **1a-g** and **2a-e** in deuteriodimethyl sulfoxide (Tables 1,2) and for compounds **1d**, **1f**, and **2b** in deuteriotrifluoroacetic acid (Table 3).

The  $\text{C}_2=\text{O}$  carbon signals of the **A** form were assigned by the  $^3\text{J}$  coupling between the  $\text{N}_1\text{-CH}_3$  proton and

$\text{C}_2=\text{O}$  carbon and between the  $\text{N}_1\text{-CH}_3$  proton and  $\text{C}_{8a}$  carbon in compounds **1c**, **2d**, and **2e** (Chart 2). On the other hand, the  $\text{C}_3$  carbon signals of the **A** form were assigned by the  $^2\text{J}$  coupling between the hydrazone CH proton and  $\text{C}_3$  carbon, although no  $^3\text{J}$  coupling was observed between the hydrazone CH proton and  $\text{C}_2=\text{O}$  carbon (Chart 3). Other carbon signals of the tautomer **A** were normally assigned by the  $^2\text{J}$  and  $^3\text{J}$  coupling data,

Table 1  
Carbon Chemical Shifts for Compounds **1a-g** in Deuteriodimethyl Sulfoxide

Carbon	Chemical Shift ( $\delta$ ppm)											
	<b>1a</b> A	<b>1b</b> A	<b>1c</b> A	A	<b>1d</b> B	A	<b>1e</b> B	A	<b>1f</b> B	A	<b>1g</b> B	
$\text{C}_2=\text{O}$	154.6	154.5	154.0	154.7	154.7	155.0	155.2	154.9	155.2	154.5	154.7	
$\text{C}_3$	148.4	148.4	147.0	149.4	150.7	149.9	151.3	149.9	151.1	149.4	150.9	
$\text{C}_{4a}$	131.6	131.6	131.9	130.9	132.6	132.2	131.9	131.2	133.0	130.9	132.7	
$\text{C}_5$	128.5	128.4	129.2	128.7	128.7	128.9	129.0	129.1	129.2	128.2	128.3	
$\text{C}_6$	123.7	123.7	124.0	123.5	123.5	124.1	123.9	124.1	124.0	123.6	123.4	
$\text{C}_7$	130.7	130.6	131.0	130.6	129.7	130.8	129.8	131.3	130.3	130.1	129.1	
$\text{C}_8$	115.5	115.4	114.8	115.6	115.3	115.9	115.7	115.9	115.8	115.3	115.2	
$\text{C}_{8a}$	132.0	131.9	133.1	132.1	131.7	131.4	133.1	132.3	131.2	131.4	131.4	
$\text{C}_1'$	145.7	145.7	145.7	144.9	145.7	145.0	145.9	147.6	148.5	140.9	141.8	
$\text{C}_2'$	112.0	112.2	112.2	113.4	112.2	99.6	99.2	113.9	112.8	114.0	113.0	
$\text{C}_3'$	130.7	130.6	130.7	133.9	134.1	160.9	160.8	131.5	131.3	129.8	129.7	
$\text{C}_4'$	120.8	120.7	120.8	121.7	119.8	106.5	106.5	123.4	121.6	129.8	129.3	
$\text{C}_5'$	134.7	134.6	134.6	131.0	131.0	130.6	130.6	131.5	131.3	129.8	129.7	
$\text{C}_6'$	114.2	114.1	114.1	112.6	111.7	106.3	106.3	113.9	112.8	114.0	113.0	
Hydrazone C	125.3	125.3	125.6	123.6	—	122.7	—	124.9	—	121.4	—	
Diazenyl C	—	—	—	—	131.9	—	130.8	—	133.7	—	129.5	
Ester $\text{C}=\text{O}$ [a]	—	—	—	—	—	—	—	—	—	—	—	
Ester $\text{CH}_3$ [a]	—	—	—	—	—	—	—	—	—	—	—	
Ester $\text{C}=\text{O}$ [b]	166.7	166.3	166.4	—	—	—	—	165.8	166.0	—	—	
Ester $\text{CH}_2$ [b]	—	60.8	60.8	—	—	—	—	60.7	60.5	—	—	
Ester $\text{CH}_3$ [b]	52.1	14.1	14.1	—	—	—	—	14.7	14.8	—	—	
$\text{N}_1\text{-CH}_3$	—	—	29.1	—	—	—	—	—	—	—	—	
<i>m</i> - $\text{OCH}_3$	—	—	—	—	—	55.6	55.4	—	—	—	—	
<i>p</i> - $\text{CH}_3$	—	—	—	—	—	—	—	—	—	20.4	20.3	

[a] Ester group on the hydrazone carbon. [b] Ester group on the side chain benzene ring.

Table 2  
Carbon Chemical Shifts for Compounds **2a-e** in Deuteriodimethyl Sulfoxide

Carbon	Chemical Shift ( $\delta$ ppm)								
	<b>2a</b>	<b>2b</b>		<b>2c</b> [c]	<b>2d</b>	<b>2e</b>			
	A	B	A	B	A	A	A		
C <sub>2</sub> =O	153.5	154.6	153.5	154.6	153.8	153.2	153.3		
C <sub>3</sub>	148.8	148.8	148.7	149.0	152.2	150.4	151.0		
C <sub>4a</sub>	131.2	131.1	131.2	131.0	131.9	132.4	132.3		
C <sub>5</sub>	129.0	129.0	128.7	129.0	129.2	130.1	129.8		
C <sub>6</sub>	123.9	123.7	123.8	123.6	123.5	124.0	123.7		
C <sub>7</sub>	131.7	131.7	131.6	131.7	131.5	132.1	131.5		
C <sub>8</sub>	115.6	115.6	115.7	115.6	115.6	115.1	114.8		
C <sub>8a</sub>	132.1	132.1	132.3	132.3	132.5	133.7	133.5		
C <sub>1'</sub>	144.7	144.4	144.7	144.4	144.8	148.9	140.9		
C <sub>2'</sub>	112.6	112.6	112.8	112.8	113.5	113.8	114.0		
C <sub>3'</sub>	130.6	130.6	130.7	130.6	133.9	125.8	129.6		
C <sub>4'</sub>	121.6	121.7	121.5	121.6	121.5	141.2	131.0		
C <sub>5'</sub>	134.9	134.9	134.8	134.7	131.0	125.8	129.0		
C <sub>6'</sub>	114.4	114.3	114.4	114.3	112.6	113.8	114.0		
Hydrazone C	130.7	—	130.8	—	129.8	133.0	127.6		
Diazenyl C	—	130.7	—	130.8	—	—	—		
Ester C=O [a]	164.7	164.7	164.7	161.5	163.7	163.3	164.0		
Ester CH <sub>3</sub> [a]	52.2	52.4	52.1	52.2	52.1	52.4	51.8		
Ester C=O [b]	166.9	166.8	166.5	166.4	—	—	—		
Ester CH <sub>2</sub> [b]	—	—	60.9	61.1	—	—	—		
Ester CH <sub>3</sub> [b]	52.2	52.2	14.0	14.1	—	—	—		
N <sub>1</sub> -CH <sub>3</sub>	—	—	—	—	—	29.2	29.0		
<i>p</i> -CH <sub>3</sub>	—	—	—	—	—	—	20.3		

[a] Ester group on the hydrazone carbon. [b] Ester group on the side chain benzene ring. [c] Carbon signals due to the tautomer **B** were too small to be assigned.

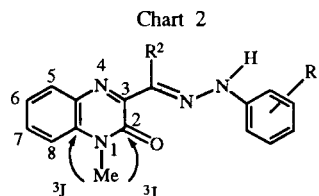
Table 3  
Carbon Chemical Shifts for Compounds **1d**, **1f**, and **2b** in Deuteriotrifluoroacetic Acid

Carbon	Chemical Shift ( $\delta$ ppm)		
	<b>1d</b>	<b>1f</b>	<b>2b</b>
	B	B	B
C <sub>2</sub> =O	155.3	155.1	154.4
C <sub>3</sub>	146.4	146.6	147.3
C <sub>4a</sub>	123.3	123.2	122.3
C <sub>5</sub>	119.3	119.7	120.5
C <sub>6</sub>	127.9	128.0	128.1
C <sub>7</sub>	131.8	132.5	133.9
C <sub>8</sub>	117.0	117.0	116.7
C <sub>8a</sub>	128.9	129.4	130.3
C <sub>1'</sub>	141.0	144.3	142.2
C <sub>2'</sub>	116.6	116.3	117.6
C <sub>3'</sub>	136.2	131.6	131.6
C <sub>4'</sub>	128.0	127.7	128.2
C <sub>5'</sub>	130.7	131.6	135.3
C <sub>6'</sub>	115.1	116.3	117.4
Hydrazone C	—	—	—
Diazenyl C	121.3	122.5	118.2
Ester C=O [a]	—	—	163.3
Ester CH <sub>3</sub> [a]	—	—	53.8
Ester C=O [b]	—	169.2	168.6
Ester CH <sub>2</sub> [b]	—	63.1	63.1
Ester CH <sub>3</sub> [b]	—	12.1	12.4

[a] Ester group on the hydrazone carbon. [b] Ester group on the side chain benzene ring.

and the carbon signals of the tautomer **B** were also assigned by the same method as the above.

In general, the C<sub>2</sub>-C<sub>8a</sub> and C<sub>1'</sub>-C<sub>6'</sub> carbon signals of the tautomer **A** or **B** were observed in a similar magnetic field among compounds **1a-g** and among compounds **2a-e**, except for the C<sub>1'</sub>-C<sub>6'</sub> carbon signals of compounds **1e** (R<sup>1</sup> = *m*-OCH<sub>3</sub>) and **1g** (R<sup>1</sup> = *p*-CH<sub>3</sub>). The chemical shifts due to the C<sub>2</sub>=O, C<sub>3</sub>, hydrazone, and diazenyl carbons are summarized in Table 4, showing that the C<sub>2</sub>=O carbon signals are observed in a lower magnetic field than the C<sub>3</sub> carbon signals in the deuteriodimethyl sulfoxide media of compounds **1a-g** and **2a-e**, and that the hydrazone carbon signals are observed in a higher magnetic field than the



**1c** R<sup>1</sup> = *o*-COOEt, R<sup>2</sup> = H  
**2d** R<sup>1</sup> = *p*-NO<sub>2</sub>, R<sup>2</sup> = COOMe

**2e** R<sup>1</sup> = *p*-Me, R<sup>2</sup> = COOMe

Carbon	Chemical Shift ( $\delta$ ppm)		
	<b>1c</b>	<b>2d</b>	<b>2e</b>
C <sub>2</sub> =O	154.0	153.2	153.3
C <sub>8a</sub>	133.1	133.7	133.5
C <sub>3</sub>	147.0	150.4	151.0

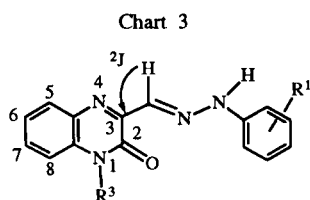
Table 4

Selected Carbon Chemical Shifts for the Hydrazone Imine **A** and Diazenylenamine **B** Tautomers of Compounds **1** and **2** in Deuteriodimethyl Sulfoxide

Carbon	Chemical Shift ( $\delta$ ppm)			
	in DMSO- $d_6$		in TFA- $d_1$	
	Compounds 1	Compounds 2	Compounds 1	Compounds 2
	A	B	A	B
$C_2=O$	155.0-154.0	155.2-154.7	153.8-153.2	154.6 [a]
$C_3$	149.9-147.0	151.3-150.9	152.2-148.7	149.0-148.8
Hydrazone C	125.6-121.4	—	133.0-127.6	—
Diazenyl C	—	133.7-129.5	—	130.8-130.7
				Compounds 1
				Compounds 2
				B
				B

[a] Value for compounds **2a** and **2b**. [b] Value for compound **2b**.

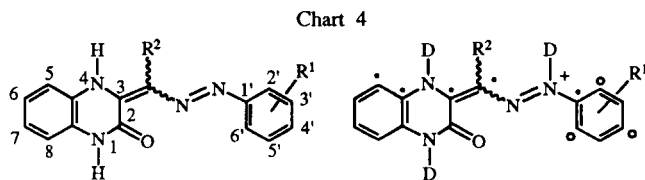
diazenyl carbon signals in the deuteriodimethyl sulfoxide media of compounds **1a-g**.



**1a-g**

Carbon	Chemical Shift ( $\delta$ ppm)
$C_2=O$	155.0 - 154.0
$C_{8a}$	133.1 - 131.4
$C_3$	149.9 - 147.0

Chart 4 shows the difference of the carbon chemical shifts between the diazenylenamine tautomer in deuteriodimethyl sulfoxide and the diazenylenamine tautomer in deuteriotrifluoroacetic acid for compounds **1d**, **1f**, and **2b**. From these data, a considerable shielding of the  $C_{4a}$  (8.7-9.8 ppm),  $C_5$  (8.5-9.5 ppm), and diazenyl carbons (10.6-12.6 ppm) was found together with a shielding of the  $C_{1'}$  carbon (2.2-4.7 ppm). Moreover, a deshielding was observed for the  $C_{2'}$  (3.5-4.8 ppm),  $C_{4'}$  (6.1-8.2 ppm), and

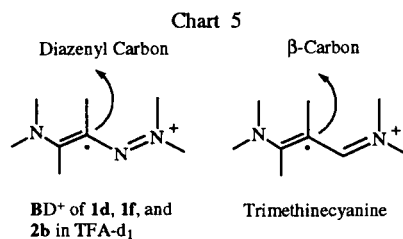
**B** in DMSO- $d_6$ **BD<sup>+</sup>** in TFA- $d_1$ 

- Means shift to higher magnetic field
- Means shift to lower magnetic field

Difference of Carbon Chemical Shifts ( $\delta$ ) between **B** in DMSO- $d_6$  and **BD<sup>+</sup>** in TFA- $d_1$ 

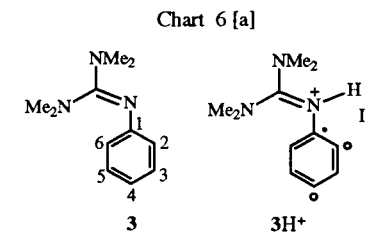
Carbon	<b>1d</b>	<b>1f</b>	<b>2b</b>
$C_3$	4.3	4.5	1.7
$C_{4a}$	9.3	9.8	8.7
$C_5$	9.4	9.5	8.5
$C_6$	4.4	4.0	4.5
$C_{1'}$	4.7	4.2	2.2
$C_{2'}$	4.4	3.5	4.8
$C_{4'}$	8.2	6.1	6.6
$C_{6'}$	3.4	3.5	3.1
Diazenyl C	10.6	11.2	12.6

$C_{6'}$  (3.1-3.5 ppm) carbons (Chart 4). These shielding and deshielding would be connected with the formation of the azo *N*-deuterized species **BD<sup>+</sup>** (Chart 4), which is supported by the results of the  $^1H$ -nmr study for *m*- and *p*-substituted compounds **1** (Scheme 2) [1,2]. The following  $^{13}C$ -nmr studies (Charts 5,6) also sustain the formation of the deuterized species **BD<sup>+</sup>** from compounds **1d**, **1f**, and **2b**. Namely, the results for the shielding of the diazenyl carbon in compounds **1d**, **1f**, and **2b** are similar to those for the shielding of the  $\beta$ -carbon in trimethinecyanine (Chart 5) [8]. In addition, the  $C_1$  carbon of compound **3H<sup>+</sup>** (Chart 6) was shielded (3.4 ppm) in comparison with that of compound **3**, while the  $C_2$  and  $C_4$  carbons of compound **3H<sup>+</sup>** were deshielded (1.9 and 5.3 ppm) when compared with those of compound **3** [8]. These shielding and deshielding data on the phenyl carbons of compound **3H<sup>+</sup>** are also similar to those of the azo *N*-deuterized species **BD<sup>+</sup>** (Chart 4).

**BD<sup>+</sup>** of **1d**, **1f**, and **2b** in TFA- $d_1$ 

Trimethinecyanine

- Means shift to higher magnetic field



- Means shift to higher magnetic field
- Means shift to lower magnetic field

Carbon	Chemical Shift ( $\delta$ )		Difference in $\delta$
	<b>3</b>	<b>3H<sup>+</sup></b>	
$C_1$	151.3	147.9	3.4
$C_2$	114.4	116.3	1.9
$C_4$	119.6	124.9	5.3

[a] Reference [8].

## EXPERIMENTAL

The nmr (HMBC and HMQC) spectra of compounds **1a-g** and **2a-e** were measured at 30° with a Varian XL-400 spectrometer at 400 MHz.

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