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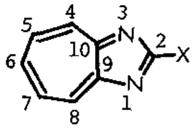
THE SUBSTITUENT EFFECT AND ASSIGNMENT OF THE ^{13}C-NMR SPECTRA OF SOME 2-SUBSTITUTED 1,3-DIAZAZULENES

Hitoshi Takeshita* and Hiroaki Mametsuka
Research Institute of Industrial Science, 86, Kyushu University,
Hakozaki, Fukuoka 812, Japan

Abstract —— The ^{13}C-NMR spectral signals of 1,3-diazazulene derivatives were unequivocally assigned by aids of ^{2}H and ^{15}N labellings. Variation of the C-2 substituents caused no appreciable effect on the chemical shifts of C-5 and C-9.

The ^{13}C-NMR spectrum is a powerful tool to study the fine structures of organic compounds, and a number of data on various compounds have been accumulated. But, as far as nonbenzenoid-aromatic compounds are concerned, still relatively small number of studies have been published to date. In connection with the study on the synthesis of zoathoxanthins[1] and paragracines,[2] we needed the NMR spectra of the 1,3-diazazulene derivatives, and we have carried out the measurements on a series of derivatives. The 1,3-diazazulenes carry nitrogens at the most electron-rich positions of the azulene skeleton, and in fact a dipolar structure is contributed in substantially as judged on the dipole moment measurement, $\mu=4.03$ D.[3] After a report by S. Ito et al.[4] in 1971, no other ^{13}C-NMR of 1,3-diazazulenes has been recorded despite they belong to a fundamental non-alternant conjugate system until a recent paper by Mathias and Overberger[5] which described an assignment of the ^{13}C-NMR spectra of two 1,3-diazazulenes. We will herein report our works to revise a part of their assignment.



The NMR spectra of 1,3-diazazulene (**1**:X=H) and some 2-substituted derivatives (**2a**–**g**) is compiled in Table 1.[6] Most of the samples were measured in $CDCl_3$, but some were measured in CD_3SOCD_3. The assignment of chemical shifts is based on the mutual comparisons, the measurements on the 4,6,8-trideuterio derivatives of **1**, **2a** (X=OMe), **2c** (X=NMe_2), **2e** (X=SMe), **2f** (X=OH), and **2g** (X=SH), and on the 1,3-di-^{15}N-derivatives of **1**, **2a**, **2c**, and **2e**. First of all, the signals of **1** appeared, from high to low field, C-5, C-4, C-6, C-9 and C-2, in the same order to the asignment by Overberger,[5] with the figures showing a good coincidence to the papers.[4,5] However, the chemical shifts of **2q** appeared in an order of C-4, C-6, C-5, C-9 and C-2, showing a contradiction with Overberger's results. They have made the assinment by use of 2-^{13}C-enriched derivative of **1**, but the assignment of **2q** seems to be deduced by an analogy. Our revised assignment is based on the folowing experiments.

Thus, Table 1 shows that throughout the series of compounds, the chemical shifts of C-5 and C-9 are nearly constant, while the others of the signals suffered a considerable effect due to the C-2 substituents. This must be reasonable since C-4, C-6 and C-8 are opposite terminals to C-2 in a formal conjugate system.

Table 1. The ^{13}C-NMR Chemical Shifts of Some 1,3-Diazazulene Derivatives (in $CDCl_3$ or CD_3SOCD_3).

	X	C-2	C-4	C-5	C-6	C-9
1	H	168.2	136.2	133.9	139.3	162.4
2a	OMe	179.3	130.4	134.9	134.6	163.6
2b	NHMe	175.1	125.2	134.9	130.4	165.2
2c	NMe_2	171.8	124.8	134.7	129.6	165.5
2d	Ph	176.7	129.4	134.2	137.4	163.9
2e	SMe	182.4	130.7	134.6	135.9	163.4
2f	$SCH_2CH=CH_2$	181.4	130.8	134.5	135.9	163.4
2g	$SCH_2C≡CH$	179.9	131.4	134.6	136.5	163.4
2h	SCH_2Ph	181.6	130.9	134.5	135.9	163.5
2i	$SCH_2C_6H_4Me$-p	181.7	130.8	134.5	135.9	163.5
2j	$SCH_2C_6H_4NO_2$-p	180.2	131.4	134.7	136.5	163.4
2k	SCH_2COOMe	179.9	131.5	134.6	136.5	163.4
2m	SCH_2COOEt	180.0	131.4	134.6	136.4	163.4
2n	Cl	168.6	135.2	134.7	139.3	162.7
2o	OH*	166.0	121.3	137.9	130.9	157.4
2p	NH_2*	175.5	123.7	134.4	129.7	165.0
2q	SH*	188.3	122.9	138.2	133.0	158.3

The solvent dependencies of the chemical shifts were then examined with **1**, **2a** and **2e**, but except in the case of CF_3COOD, no appreciable change of chemical shifts can be observed. This might be attributable to a substantial contribution of the polarized structures for **1** and **2** even in the non-polar solvents. The ^{13}C-NMR spectra in CF_3COOD caused a considerable change of the chemical shifts for all the carbon atoms, but the substituent effect on the chemical shift, $\Delta\delta_{\mathbf{2}}=\delta_{\mathbf{1}}-\delta_{\mathbf{2}}$, in this solvent, of C-5 [$\Delta\delta_{\mathbf{2a}}=-2.2$, $\Delta\delta_{\mathbf{2e}}=-1.9$] and C-9 [$\Delta\delta_{\mathbf{2a}}=-1.7$, $\Delta\delta_{\mathbf{2e}}-2.1$] were again smaller than those of C-4 [$\Delta\delta_{\mathbf{2a}}=8.3$, $\Delta\delta_{\mathbf{2e}}=8.7$] and of C-6 [$\Delta\delta_{\mathbf{2a}}=6.0$, $\Delta\delta_{\mathbf{2e}}=4.9$] as calculated from the figures in Table 2. These also supported our assignment.

Table 2. The Solvent Dependence of the Chemical Shifts (δ) of Some 1,3-Diazazulene Derivatives.

		C-2	C-4	C-5	C-6	C-9
1:X=H	CCl_4	168.4	135.2	132.4	137.6	162.3
	$CDCl_3$	168.2	136.2	133.9	139.3	162.4
	C_6D_6	169.2	135.7	132.8	138.0	163.0
	CD_3COCD_3	169.0	136.7	134.6	140.3	163.2
	C_5D_5N	169.0	136.3	134.0	139.6	163.0
	CD_3OD	167.2	137.8	136.6	142.4	162.3
	CD_3SOCD_3	167.8	136.1	134.3	140.1	161.8
	CF_3COOD	155.8	145.3	142.7	152.1	154.4
2e:X=SMe	CCl_4	182.4	129.8	133.3	134.3	163.2
	$CDCl_3$	182.4	130.7	134.6	135.9	163.4
	C_6D_6	183.6	130.3	133.8	134.8	164.1
	CD_3COCD_3	182.7	131.6	135.6	137.2	164.2
	C_5D_5N	182.5	131.1	134.9	136.4	163.9
	CD_3OD	182.3	132.3	137.0	138.7	163.8
	CD_3SOCD_3	180.6	130.1	135.2	137.0	162.7
	CF_3COOD	173.6	136.6	144.6	147.2	156.5
2a:X=OMe	CCl_4	179.4	129.2	133.5	132.9	163.4
	$CDCl_3$	179.3	130.4	134.9	134.6	163.6
	C_6D_6	180.6	130.0	134.1	133.5	164.3
	CD_3COCD_3	180.3	130.9	135.8	135.6	164.4
	C_5D_5N	179.9	130.6	135.2	135.0	163.9
	CD_3OD	179.1	131.9	137.3	137.4	163.7
	CD_3SOCD_3	178.6	130.3	135.3	135.3	162.8
	CF_3COOD	167.7	137.0	144.9	146.1	156.1

Finnaly, the assignment was assured by the isotope labellings: The ^{13}C-NMR spectra of 4,6,8-trideuterio derivative of **2a**, illustrated in Fig. 1, clearly retained the *signals at δ 138.2, 158.3 and 188.3, to which we assigned as C-5, C-9, and C-2.* In addition, the observations of the ^{15}N-^{13}C-couplings by the ^{13}C-NMR measurements on the di-^{15}N-labelled compounds[7] of **1**, **2a**, **2c**, and **2e**. The NMR of this enriched sample of **2e** is illustrated in Fig. 2.

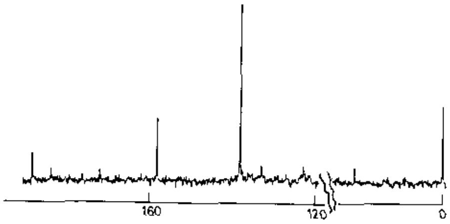


Fig. 1: The ^{13}C-NMR Spectrum of 4,6,8-Trideuterio Derivative of **2g** (in CD_3SOCD_3)

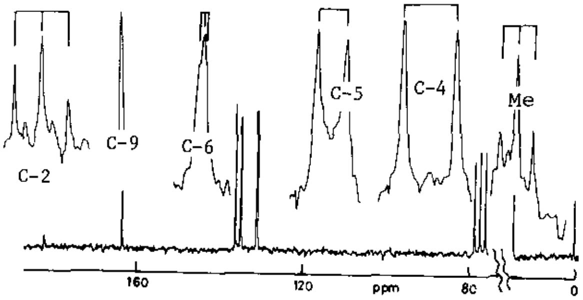


Fig. 2: The ^{13}C-NMR spectrum of Di-^{15}N-Derivative of **2e** (in $CDCl_3$)

Table 3 summarized the results of $^{n}J(^{15}N-^{13}C)$.

Table 3. The The $^{n}J(^{15}N-^{13}C)$ of some Di-^{15}N-Azazulenes (Hz).

$^{n}J(C-x)$	$^{1}J(C-2)$	$^{1}J(C-9)$	$^{2}J(C-4)$	$^{3}J(C-5)$	$^{4}J(C-6)$	$^{3}J(Me)$
1	4.0	1.5	7.5	4.0	0	-
2a	2.6	1.2	8.1	4.4	0	2.3
2c	3.2	2.0	8.5	4.4	0	1.6
2e	4.1	0	8.1	4.4	0.5	2.4

The above evidences are consistent in each other, and the assignment deduced should be true. Detailed features of the spectra will be discussed elsewhere.

References and Notes

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2. Y. Komoda, S. Kaneko, M. Yamamoto, M. Ishikawa, A. Itai, and Y. IItaka, Chem. Pharm. Bull. Japan, 1975, 23, 2464.
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4. J. Tsunetsugu, S. Ito, H. Ohtani, T. Nishida, and K. Kushida, 'Abstract Papers of Third International Symposium of Heterocyclic Chemistry', p 523 (Sendai, Aug., 1971).
5. L. J. Mathias and C. G. Overberger, J. Org. Chem., 1978, 43, 3526.
6. The ^{13}C-NMR spectra were obtained by measurements with an FX 100 Model Spectrometer (JEOL Co.) at 25 MHz with FT mode.
7. The ^{15}N-NMR of **2e** in $CDCl_3$ exhibited a signal at 111.4 ppm up field from the external standard, $NH_4\underline{N}O_3$. An ^{15}N-NMR study on the **1** and **2** will be a subject of another paper.

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