^{13}C NMR Spectra of 1,3-Dithiolan-2-ylium Ions and 2-Alkylidene-1,3-dithiolanes

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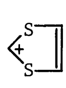
Synopsis. ^{13}C NMR spectra of various 2-substituted 1,3-dithiolan-2-ylium perchlorates **5** as well as 2-alkylidene-1,3-dithiolanes **6** are measured. Chemical shifts induced by protonation of **6** to form **5** are compared with those found with the unsaturated analogues, 1,3-dithiolylium ions, implying the aromatic charge delocalization in the latter ions.

1,3-Dithiolylium ion **1** is an unsaturated five-membered ring cation which possesses potential aromatic sextet. The stability of this ion is usually attributed to this 6π-electron delocalization (**1a**).[1] The NMR spectral data of this class of cations have been considered to support this view in one paper[2] while the other workers[3] rationalized the observed ^{13}C chemical shifts only by the sulfur conjugation (**1b**). The former paper[2] examined both ^{1}H and ^{13}C NMR spectra of **1** and the saturated analogue, 1,3-dithiolanylium ion **2**, as well as their neutral precursors. The signal of 2-H of **1** appeared at a lower field than that of **2**, whereas the chemical shift of 2-C of **1** is much smaller than that of **2**, suggesting the aromatic ring current and charge delocalization in **1**. On the other hand, the latter workers[3] compared ^{13}C NMR spectra of 2-substituted derivatives of **1** with those of their deprotonated derivatives; e. g., **3** and **4**. Chemical shift differences between **3** and **4** were found to be much greater at 2-C than at 4-C.



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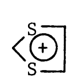
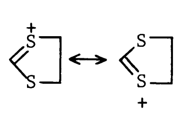


1a



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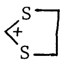

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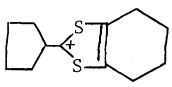

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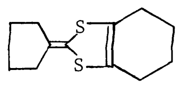

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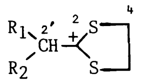
In the present investigation, we have measured ^{13}C NMR spectra of substituted 1,3-dithiolan-2-ylium ions **5** and 2-alkylidene-1,3-dithiolanes **6** in order to examine the conclusion deduced from the similar comparison between **3** and **4**. Perchlorates of **5** were prepared from acyl chlorides and 1,2-ethanedithiol and converted to **6** by the treatments with triethylamine.[4] ^{13}C FT NMR spectra were recorded at 27 °C on a JNM-FX 100 spectrometer operating at 25.05 MHz.[5] Spectra of **5** and **6** were measured as 5—10% solutions in CF3COOH-CF3COOD and CDCl3, respectively. Results are summarized in Table 1.



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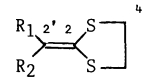

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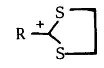

5

a, $R_1=R_2=H$ **b**, $R_1=H$, $R_2=CH_3$ **e**, $R=(CH_3)_3C$
c, $R_1=R_2=CH_3$ **d**, $R_1=H$, $R_2=C_6H_5$ **f**, $R=C_6H_5$
g, $R=p\text{-}CH_3OC_6H_4$

Table 1. ^{13}C Chemical Shifts of **5** and **6**[a)]

No.	R(R1, R2)	2-C	4-C	2-C′ [b)]	Others
2[c)]	H	221.4	46.4		
5a	CH_3	245.0	47.8	24.4	
5b	CH_3CH_2	253.4	46.8	34.0	15.6
5c	$(CH_3)_2CH$	259.1	46.8	41.7	28.5
5e	$(CH_3)_3C$	264.1	46.5	48.5	32.8
5d	$C_6H_5CH_2$	242.6	46.8	45.2	130.5, 131.5, 135.0
5f	C_6H_5	234.6	45.4	143.3	132.0, 132.3, 144.0
5g	$p\text{-}CH_3OC_6H_4$	225.5	44.2	126.6	57.9, 118.1, 136.8, 174.3
6a	(H, H)	144.3	38.4	99.3	
		(100.7)	(9.4)	(−74.9)	
6b	(H, CH_3)	135.2	36.9, 37.2	110.6	9.3
		(118.2)	(9.7)	(−76.6)	
6c	(CH_3, CH_3)	127.1	37.9	119.1	24.2
		(132.0)	(8.9)	(−77.4)	
6d	(H, C_6H_5)	137.8	35.4, 39.5	115.5	125.5, 127.0, 128.0, 137.1
		(104.8)	(9.3)	(−70.3)	

a) ppm downfield from internal TMS. Values in parentheses show the chemical shift differences between **5** and **6**. b) The carbon next to 2-C. c) Taken from reference 2.

Assignments of signals were made by comparisons with those of relevant compounds.

Resonance of 2-C of dithiolanylium ions **5** occurs at the lowest field reflecting a positive charge. Among the chemical shifts of 2-C of **5**, the largest is that of **5e** (R=*t*-Bu), decreasing in the order **5e**(*t*-Bu)>**5c**(*i*-Pr)>**5b**(Et)>**5a**(Me)>**5d**(PhCH$_2$). This order coincides with that of electron-donating ability of alkyl groups to the positive center, e. g., in terms of the σ_p^+ substituent constants, and indicates decreasing order of the charge density at the positive carbon. The 2-phenyl and 2-(*p*-methoxyphenyl) cations (**5f** and **5g**) have the 2-C signals at still higher field.

2-Alkyl-1,3-dithiolanylium ion **5** is formed by protonation of 2-alkylidene-1,3-dithiolane **6**. The protonation causes large downfield (100—132 ppm) and upfield (70—77 ppm) shifts at 2-C and 2-C′ (the carbon next to 2-C), respectively, as given in parentheses in Table 1. The chemical shift of 4-C (5-C) changes only by about 9 ppm. The upfield shift of 2-C′ must mostly be due to the hybridization change from sp^2 to sp^3. The downfield shifts at 2-C and 4-C come primarily from a positive charge of the cation **5**. Similar changes in the chemical shifts of the unsaturated analogues (**3** and **4** and related dithiole derivatives) were found to be 74—89, −74—81, and 28 ppm at 2-C, 2-C′, and 4-C, respectively.[3] The changes at 2-C′ are much the same between the dithiole and dithiolane derivatives (70—80 ppm upfield shift), as expected for the same hybridization change. However, downfield shifts at 2-C and 4-C of dithiolylium ions are 30—40 ppm smaller and about 20 ppm larger than those of dithiolanylium ions, respectively. This indicates that the charge density in dithiolylium ion **1** is smaller at 2-C while greater at 4-C as compared with that in dithiolanylium ion **2**. That is, the positive charge in **1** delocalizes extensively involving the 4 and 5 carbons.

^{13}C NMR data presented by Meier et al.[3] should be taken as indicating that the positive charge delocalizes over the whole ring system of dithiolylium ion (**1a**), contrary to their conclusion.

References

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2) K. Sakamoto, N. Nakamura, M. Ōki, J. Nakayama, and M. Hoshino, *Chem. Lett.*, **1977**, 1133.

3) U. Timm, U. Plücken, H. Petersen, and H. Meier, *J. Heterocycl. Chem.*, **16**, 1303 (1979).

4) T. Okuyama, W. Fujiwara, and T. Fueno, *Bull. Chem. Soc. Jpn.*, in press.

5) We thank Y. Terawaki for recording the spectra.