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^{13}C NMR STUDY OF 1,3,4,6-TETRAAZA-6a(S^{IV})THIAPENTALENIUM TETRAFLUOROBORATE AND REFERENCE PRECURSOR, 5-(1-IMINOETHYLMETHYLAMINO)-3-METHYL-1,2,4-THIADIAZOLE

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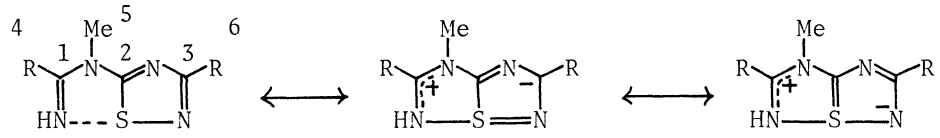
^{13}C Chemical shifts of 1,2,3,5,6-pentamethyl-1,3,4,6-tetraaza-6a(S^{IV})thiapentalenium tetrafluoroborate and a reference precursor, 5-(1-iminoethylmethylamino)-3-methyl-1,2,4-thiadiazole, were assigned by comparison with their derivatives. Chemical shifts of all the carbons of the former lie at upfield to those of the latter.

Chemistry of hypervalent molecules has acquired recent attention partly due to the work on σ-sulfuranes[1] and σ-phosphoranes.[2] On the other hand, significant progress on π-sulfuranes has not been so prominent after the structural determination of thiathiophthenes probably due to the complex nature of the π-sulfurane. Concerning this topic, we reported 1,3-dipolar cycloaddition of arylcyanamides with Hector's base and a subsequent bond switch at the π-hypervalent sulfur.[3] Moreover, the nature of intramolecular S···N interaction was shown to be a charge transfer type through the π-hypervalent sulfur.[4] Recently, we prepared 5-(1-iminoethylmethylamino)-3-methyl-1,2,4-thiadiazole (1a), 1,2,3,5,6-pentamethyl-1,3,4,6-tetraaza-6a(S^{IV})thiapentalenium tetrafluoroborate (2a), and their derivatives. The structure of 1a and 2a was elucidated by X-ray crystallography and the N···S bond lengths are shown in the text.[5] This paper describes determination and comparison of ^{13}C chemical shifts of structurally related compounds, i.e., 1a and 2a.

^{13}C Chemical shifts of all carbons of 1a were assigned by comparison with those of derivatives (1b-1d) (Table 1). All ^{13}C chemical shifts of 1a, except C-1, are almost equal to those of 4 and quite different from those of 6, indicating that the structure is correctly depicted not as A but as 1. By the same token as for the previous report,[4] intramolecular charge transfer from the amidino group to the thiadiazole ring can be realized by comparison of chemical shifts of the corresponding carbons of 1a with 3 and 5 and this fact can be depicted as below.

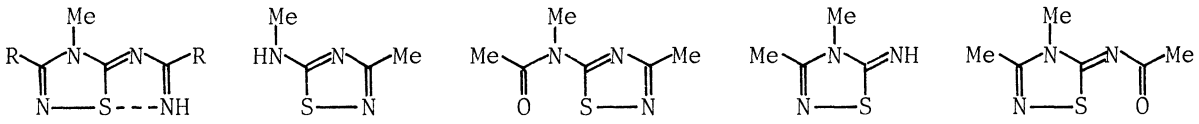


1 2.50 1.67 (Å) 1' 1''

Table 1. ^{13}C-Chemical Shifts of 1a and Related Compounds*1

Compound	Substituent		^{13}C Chemical Shifts*2					
	R^4	R^6	C-1	C-2	C-3	C-4	C-5	C-6
1a	Me	Me	161.3	177.2	166.4	23.4	36.1	19.4
1b	Me	Ph	161.4	177.2	166.1	23.3	36.1	(134.3)*3
1c	Ph	Me	165.3	177.6	166.8	(135.7)*3	38.5	19.4
1d	Ph	Ph	165.3	176.1	166.5	(135.6)*3	38.5	(134.2)*3
3			—	186.4	170.4	—	32.6	19.1
4			171.3	177.0	167.4	22.3	36.0	19.3
5			156.7	170.1	—	17.6	30.4	—
6			153.6	178.1	182.8	16.5	33.2	26.1

*1 All ^{13}C FT-NMR spectra were recorded on a JEOL PS-PFT 100 spectrometer at 25 °C (accuracy, ± 0.1 δ ; concentration $\lesssim$0.1 mmol/cm^3).
*2 δ from TMS in $CDCl_3$. *3 δ for ipso-carbon.



A 3 4 5 6

Then, ^{13}C chemical shifts of 2, dialkylated product of 1, were determined in DMSO-d_6 by comparison with appropriate derivatives (Table 2). The most remarkable fact is that all the corresponding carbons of 2a resonated at higher fields than

those of 1a in spite of the presence of a net positive charge in the molecule. The upfield shifts are quite prominent for C-2 and C-4 and that at C-6 is not so large as C-4. The chemical shift of C-3 is hardly affected and it is noteworthy that an upfield shift was observed by an introduction of a phenyl group as R^6 which is not the case with 1.

Table 2. ^{13}C Chemical Shifts of 2a and Derivatives

Compound	Substituent			^{13}C Chemical Shifts*1							
	R^6	R^7	R^8	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
2a	Me	Me	Me	157.3	164.0	165.2	12.8	33.8	16.9	30.0	31.0
2b	Ph	Me	Me	157.8	164.0	161.9	12.8	33.9	*3	31.5	31.0
2c	Ph	Et	Me	157.8	164.2	162.2	12.8	34.0	*3	41.3*2	31.1
2d	Ph	Me	Et	157.0	164.2	162.2	12.7	33.9	*3	31.6	40.0*2

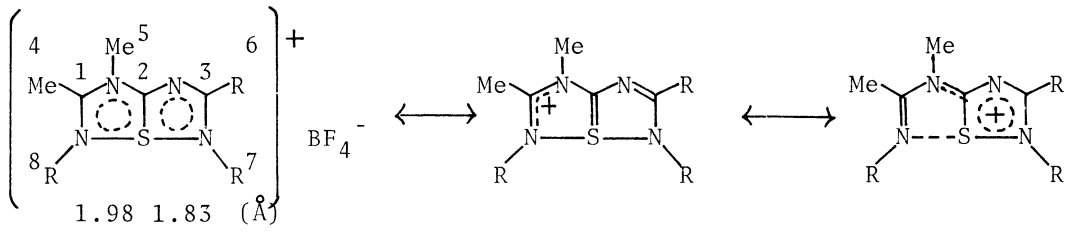
*1 δ from TMS in DMSO-d_6 *2 δ for the methylene of the ethyl group and that for the methyl of the ethyl group is 16.2 for 2c and 15.5 for 2d.
*3 δ for ipso-carobon of the phenyl group was not determined.

Table 3. Solvent Effect on ^{13}C Chemical Shifts of 1a and 2a

Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1a	DMSO-d_6	161.1	176.1	165.0	21.3	35.5	19.0		
	MeOH-d_4	162.4	177.8	167.2	21.7	36.0	18.9		
	MeCN-d_3	163.0	178.5	166.7	22.7	36.5	19.4		
2a	DMSO-d_6	157.3	164.0	165.2	12.8	33.8	16.9	30.0	31.0
	MeOH-d_4	158.5	166.3	167.0	12.9	34.4	17.2	30.5	31.3
	MeCN-d_3	158.1	165.7	166.7	13.4	34.5	17.6	30.7	31.6

This upfield shift could be due to the interaction with the solvent, i.e., DMSO. However, no actual solvent effect was observed with 1a and 2a in DMSO, methanol, and acetonitrile (Table 3).

Here the reason for the real upfield shifts from 1 to 2 should be explained. It is apparent by inspection that 2 is the best description for the compound and 2' and 2'' stand for two and five canonical forms, and hence the positive charge is distributed over the whole ring atoms except the nitrogen between the carbons 2 and 3.



2 2' 2''

Therefore, an imidazolium salt and imidazole can be a simple good model to explain the chemical shift of ring carbons of the present case. The chemical shifts of all the carbons of the imidazolium salt are shifted upfield compared with those of imidazole, and this is mainly ascribed to the decrease in the π-bond order of the N-C_α bond by a CNDO-SCF calculation.[6] The chemical shift of α-carbons of a pyridinium salt lies at a higher field compared with that of pyridine, and this is also explained similarly.[7] Accordingly, the present result is understandable by the same kind of rationalization and also by the shortening of the N—S bonds of the molecule (2) compared with those of 1, although a theoretical calculation is awaited for an exact understanding.

References

1) P. Livant and J. C. Martin, J. Am. Chem. Soc., 99, 5761 (1977), and references cited therein.

2) F. Ramirez, Acc. Chem. Res., 1, 168 (1968); F. Ramirez, Synthesis, 1974, 90.

3) K. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, Tetrahedron Lett., 1975, 455; K. Akiba, T. Tsuchiya, N. Inamoto, K. Onuma, N. Nagashima, and A. Nakamura, Chem. Lett., 1976, 723.

4) K. Akiba, T. Tsuchiya, N. Inamoto, K. Yamada, H. Tanaka, and H. Kawazura, Tetrahedron Lett., 1976, 3819.

5) K. Akiba, S. Arai, and F. Iwasaki, Tetrahedron Lett., 1978, 4117, and unpublished results.

6) R. J. Pugmire and D. M. Grant, J. Am. Chem. Soc., 90, 4232 (1968).

7) R. J. Pugmire and D. M. Grant, J. Am. Chem. Soc., 90, 697 (1968); J. P. Larkindale and D. J. Simkin, J. Chem. Phys., 55, 5048 (1971).

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