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A ^{13}C-NMR STUDY ON THE *1:1* ADDUCT OF "HECTOR'S BASE" WITH ARYLCYANAMIDES EVIDENCE FOR INTRAMOLECULAR S···N INTERACTION [1]

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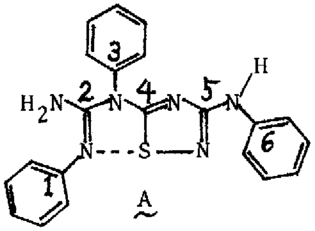
The structure of the *1:1* adduct of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines (**C**: Hector's base) with arylcyanamides was recently determined to be **A** by X-ray crystal analysis.[2] Preservation of the structure in solution was exemplified by the presence of a strong absorption at 1660 cm^{-1} both in KBr disc and in solvents (THF, $CHCl_3$, MeOH, and DMSO), being attributable to the C=N bond of the guanidino group as influenced by electron-withdrawing character of the sulfur atom.[3] According to the above mentioned results, the initially proposed structure for the *1:1* adduct has been shown to be revised as **A** and the important role of hypervalent sulfur was disclosed both in processing the reaction and in stabilizing the final product.[2] We investigated the nature of the intramolecular interaction between the nitrogen and the sulfur of the *1:1* adduct by ^{13}C-NMR spectroscopy, the result of which supports the above interpretation of the IR band and does the electron-withdrawing character of the hypervalent sulfur.

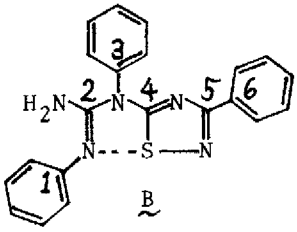
^{13}CFT-NMR spectra were recorded on a JEOL PS-PFT-100 spectrometer in DMSO-d_6 at 25 °C for the following compounds: *1:1* adducts, **A** and **B**, reference compounds for the composite part of the adduct, **C**, **D**, and **E**, and a benzoyl derivative of **C**. Chemical shifts were assigned by comparison of proton irradiated spectra and also of proton off-resonance spectra of these compounds. The results are shown in the Table.

Following facts are apparent by inspection of the Table: 1) δ values of all designated carbons of **A** and **B** are almost identical except those of C-5 and C-6, ii) δ (C-1) of **A** and **B** are apparently lower than that of **C**, iii) δ (C-3) of **A** and **B** are considerably lower than those of **C**, **D**, and **E**, iv) δ (C-4) and δ (C-5) of **A** and **B** are essentially the same as those of **D** and **E**, respectively, showing the presence of a thiadiazole ring, but a closer inspection reveals the presence of a definite signal shift of the thiadiazole ring carbons of **A** and **B** toward a higher field compared with those of **D** and **E**, and v) the signal of **F** shows a large down-field shift from that of **C** owing to the introduction of an electron-withdrawing group.

From these results, we conclude that the guanidino group of A and B behaves as an electron donor (ii and iii) and the thiadiazole ring does as its acceptor (iv) due to an intramolecular interaction (N···S). This effect can be depicted as shown in the Scheme. Present result can be realized by electron-accepting character of the hypervalent sulfur and is consistent with the proposed scheme to explain the structure determined by the X-ray analysis.[2]



A



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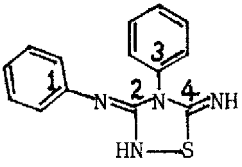
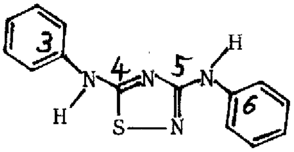
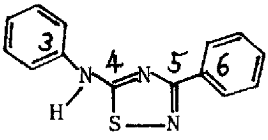


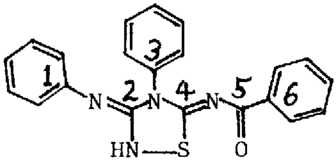
C



D



E



F

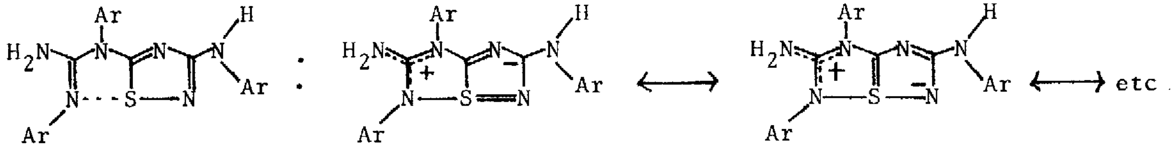
Table ^{13}C Chemical Shifts of Designated Carbons

	C-1	C-2	C-3	C-4	C-5	C-6
A	137.5	146.0	145.3	174.6	159.1	141.2
B	137.4	146.2	145.2	176.5	164.4	132.9
C	133.8	147.6	139.1	164.6		
D			139.6	175.7	161.9	138.2
E			139.7	178.8	168.3	132.6
F	133.9	147.9	138.9	178.0	174.7	134.6

Accuracies of δC (ppm downfield from internal TMS) are about ±0.1.

Solutions of about 0.2 mmol/ml in DMSO-d_6 were used.

Scheme



References

1. Chemistry of Hypervalent Sulfur, V: for Part IV, see K. Akiba, T. Tsuchiya and N. Inamoto, Tetrahedron Lett., 1877 (1976); also see literatures cited in references 1 and 2.
2. K. Akiba, T. Tsuchiya, N. Inamoto, K. Onuma, N. Nagashima and A. Nakamura, Chem. Lett., 723 (1976).
3. K. Akiba, T. Tsuchiya and N. Inamoto, Tetrahedron Lett., 455 (1975); L.J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968, p.49.