

# Characteristic coupling constants $^1J_{(^{13}\text{C}-^{13}\text{C})}$ of some mesoionic methylides containing a diphenyltetrazolium ring

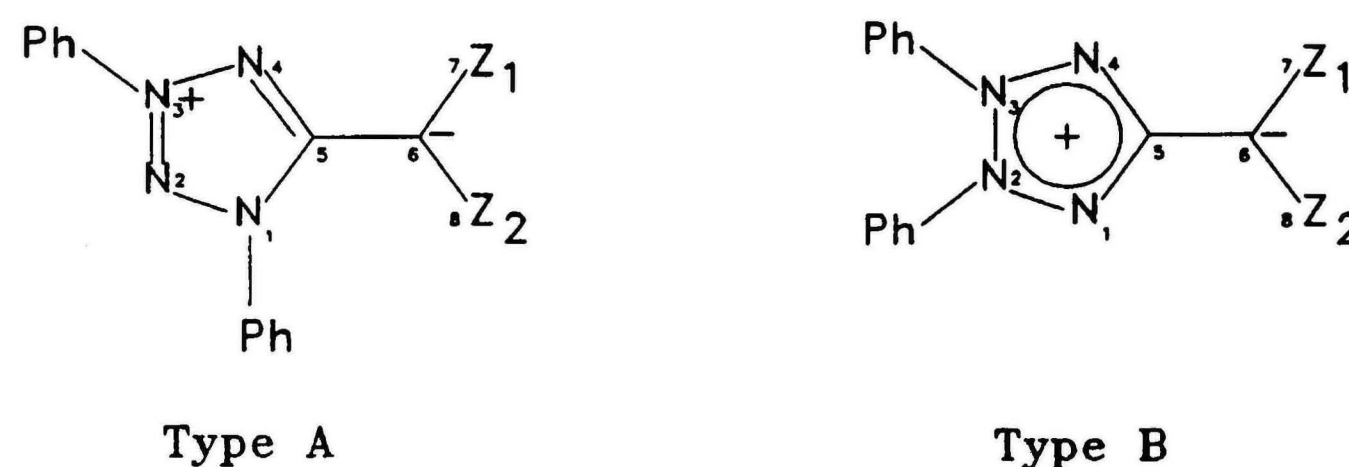
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**Abstract.**  $^1J_{(^{13}\text{C}-^{13}\text{C})}$  data are presented for some Types A and B tetrazolium methylides. The results show a large amount of double bond character for the  $\text{C}_5\text{-C}_6$  bond which is significantly reduced upon protonation. A similar decrease in bond order is noted for the  $\text{C}_6\text{-C}_8$  bond following protonation.

## 1. Introduction

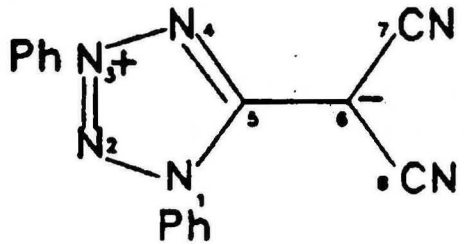
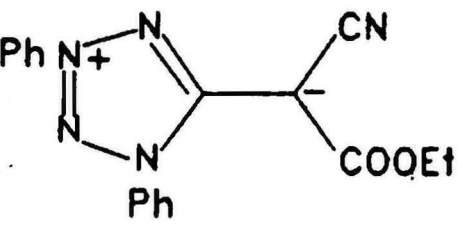
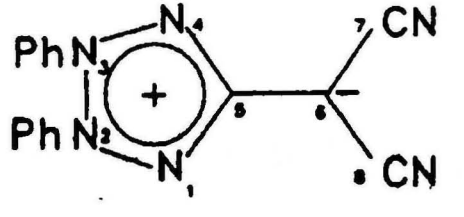
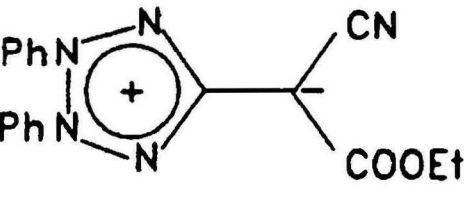
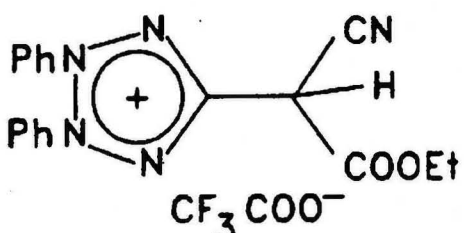
Mesoionic heterocycles are compounds with interesting structural properties [1,2]. Previously the mesoionic Type [3] and Type B [4,5] tetrazoles were investigated by  $^{13}\text{C}$ ,  $^{14}\text{N}$  and  $^{15}\text{N}$  Nuclear Magnetic Resonance (NMR) techniques. Now, the  $^1J_{(^{13}\text{C}-^{13}\text{C})}$  coupling constant measurement is used as a means of investigation for the  $\text{C}_5\text{-C}_6$  bond of some mesoionic tetrazolium methylides **1-4**. (Figure 1).



**Figure 1.** Type A and Type B mesoionic tetrazoliummethylides.

Table 1

Some  $^1J_{(13C-13C)}$  couplings (Hz) for some mesoionic Types A and B tetrazolium methylides<sup>a</sup>

Compound		$^1J_{(C5-C6)}$	$^1J_{(C6-C7)}$	$^1J_{(C6-C8)}$
1		98.9	98.6	98.6
2		90.9	91.3	93.7
3		96.1	98.5	98.5
4		92.5	b	b
5		59.6	b	65.8

a The data taken on solution in DMSO- $d_6$  with the exception of compound 4 where trifluoroacetic acid (TFA) also was used (compound 5). b Not all  $^1J_{(13C-13C)}$  couplings were determined due to a long relaxation time for the quaternary carbon atoms.

## 2. Results and discussion

The  $^1J_{(13C-13C)}$  coupling constants of the exocyclic groups for some A and B Types of mesoionic tetrazoles are presented in Table 1.

In contrast to the mesoionic 3-phenyl-1-thia-2,3,4-triazolium-5-methylides [6], both CN groups seems to be equivalent for the mesoionic tetrazole 1 [7]. Thus, just one  $^1J_{13C-13C}$  coupling constant is observed for the  $C_6-C_7$  and  $C_6-C_8$  bonds (98.9 Hz); similar values of  $^1J_{C5-C6}$  are observed for all of the compounds given in Table 1. Thus, showing that the Type A compounds 1 and 2 and Type B compounds 3 and 4 mesoionic compounds, respectively, have the same character for the  $C_5-C_6$  bonds. Unfortunately, not all  $^1J_{13C-13C}$  couplings were determined for these compounds, despite using a long measurement time, probably due to a long relaxation time for the quaternary carbon atoms.

As was demonstrated previously [7] the compound **4** is protonated in  $\text{CF}_3\text{COOH}$  solution. The proton is located on the  $\text{C}_6$  atom. It was expected that the  $\text{C}_5\text{-C}_6$  bond in the protonated compounds is closer to being a single bond rather than a double bond. Indeed, the value of the coupling constant decreases to 59.6 Hz in  $\text{CF}_3\text{COOH}$  solution thus strongly supporting the view of a decrease in the  $\text{C}_5\text{-C}_6$  bond order in this compound [8]. A similar change is noted for the  $\text{C}_6\text{-C}_7$  upon protonation.

### 3. Experimental

The compounds were obtained according to published procedures [9, 10]. All NMR measurements were made on the Bruker AM 500 spectrometer. About 0.5 M solutions of the compounds in  $\text{DMSO-d}_6$  was used as the lock. About 1% of the molar ratio of  $\text{Cr}(\text{acac})_3$  was used to decrease the relaxation delay (with the exception of  $\text{CF}_3\text{COOH}$  solution).

The standard INADEQUATE technique was applied, with a relaxation delay of 1-1.5 s and an acquisition time of *ca.* 1.2 seconds. Typically, the total experimental time was 12-24 hrs, 20000-40000 scans were acquired. A spectral resolution of 0.35 Hz/Pt was used. Generally, it was necessary to use a long experimental time, because of the long relaxation time of the quaternary carbon atoms.

### 4. Acknowledgements

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### 5. References

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